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# SYSTEMATIC SURVEY *of* RUBBER CHEMISTRY

A bibliography, with copious abstracts, of the entire literature of rubber chemistry and closely allied subjects; thoroughly indexed by authors and subjects, and completely cross-referenced; together with a patent index, and introductory chapters summarizing the present status of rubber chemistry.

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*BOOK DEPARTMENT*

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# INTRODUCTION

BY

DR. W. C. GEER

A work of reference usually embodies two essential characteristics: those of completeness and accuracy. But there is a third necessary feature too frequently missing from such documents: references should expound something of the subject-matter contained in the original articles. Title and author indexes are of little value to the research chemist unless they suggest the contents of the text. Because of the enormous amount of literature, hundreds of articles must be read in the search for information.

To make references available by reliable, though brief, analytic abstracts and by subject indexes in detail, is an achievement and a high service to investigators.

This book fulfills these requirements, and will serve not only the rubber chemist but the research chemist generally. We leave our prior art searches all too frequently to the Patent Office. Time and money may be saved by a study of these illuminating abstracts.

The rubber industry has been in recent years, through its chemists and engineers, more open in co-operative endeavor than during its entire previous history. Indeed, where the industry was formerly known as one of the most secretive, it has now passed many of its contemporaries and has become one of the most open. This contribution to the literature of rubber may justly be said to be offered as an expression of that open-mindedness which has now become so prevalent, that research work may go on more freely and contributions to the general good be more noticeable because of it.

Few volumes will stand the test of critical use more exactly than this one.



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## EXPLANATION

The object of this book is to present, as accurately and as completely as possible, a systematic survey of the field of rubber chemistry up to January 1, 1923. Abstracts of 1922 publications, appearing in 1923, are included up to the time of going to press.

This survey is the result of a page by page search of the contents of the following libraries:

John Crerar Library. Chicago.  
Library of Congress. Washington.  
New York City Library.  
Chemists' Club. New York.  
Yale University. New Haven.  
Library of the Patent Office. Washington.  
Western Reserve University. Cleveland.  
University of Illinois. Urbana.  
Engineering Societies. New York.  
B. F. Goodrich Co. Akron.  
Goodyear Tire & Rubber Co. Akron.  
Case School of Applied Science. Cleveland.  
Carnegie Institute of Technology. Pittsburgh.  
Private library of Mr. Henry C. Pearson.

A detailed list of the publications actually consulted is found in the list of journal abbreviations on page 13. This search has been limited to the Chemistry of Rubber and the attempt has been made to include all important data relative thereto, the following subjects having been omitted:

Analysis of rubber.  
Synthetic rubber.  
Physical properties of rubber.  
Rubber testing.  
Rubber botany.  
Diseases of rubber trees.  
Reclaimed rubber.

Articles dealing with these subjects have been included only when they contain data relative to molecular structure, ageing, accelerators, or similar subjects. Many old references are included from their historical value alone, such as the first patent for a pneumatic tire.



*Arrangement and Use of the Survey.*

The survey is arranged in three main divisions: Author Index, Subject Index, and Patent Index.

The *Author Index* constitutes a bibliography with the authors listed in alphabetical order. The works of each author are given in approximate chronological order, with a reference number assigned to each article or group of patents. This reference number is used for cross-indexing between the various divisions of the survey, for example, Bruni, G. (10), refers to the tenth item under G. Bruni in the Author Index. In addition to the original reference for each article or patent, references are included showing the location of abstracts and reprints as well as many discussions referring to the same in various books or reviews. Such multiplication of references furnishes an index to such libraries as may be available to the investigator, making clear the location of information at hand without the need for time-consuming searches.

By use of the many abstracting journals, it is believed that the entire literature has been fairly well covered even where the original article has not been available.

The *Subject Index* is perhaps the most valuable portion of the survey. Arranged in alphabetical order, it attempts to correlate all data relative to every chemical compound which influences vulcanization or reacts with rubber. The abstracts are indicative of the nature of the work rather than condensations of data, and in no way seek to take the place of consultation of the original publications.

The subject index also correlates data on such broad subjects as Ageing, Colloid Chemistry of Rubber, Viscosity, Depolymerization, etc. Compilations of this type, to be absolutely complete, should include all references where these subjects are even indirectly dealt with. Such completeness has been approximated by cross-indexing. Abstracts, in these cases, seek to record some one or two points of interest from the published data which might guide the searcher in choice of articles to be consulted.

The authors are listed in alphabetical order under each subject, followed by a number in parenthesis referring to the corresponding reference number in the author index. Where no abstract is given the subject is merely mentioned in the original article, the subject heading is sufficiently clear or the data are the same as shown elsewhere.

Exhaustive literature searches by chemists or patent attorneys are rare, due to the large amount of time and the great expense which they require. This survey should make all future searches more nearly complete than many so-called exhaustive searches have been in the past.

A numerical *Patent Index* is added as a matter of convenience. The reference numbers refer to the author index as before.

This survey comprises a contribution to the rubber literature, and as such may call upon the reader to make note of all errors or omissions which come to his attention, for the benefit of future editions.

Acknowledgment is made of the assistance which the authors have received from many sources and individuals. The librarians of the various libraries have given many hours of co-operation. The E. I. DuPont Co. through Messrs. W. J. Kinsman and Winfield Scott have located many missing articles in their library. Those who have written the introductory chapters have given other valuable assistance in the preparation of this survey. Finally to Dr. W. C. Geer and the B. F. Goodrich Company we acknowledge that encouragement and assistance without which publication would not have been possible.



## TEXT ABBREVIATIONS

Accel.....	Accelerator(s). Accelerated. Acceleration.
Add.....	Addition.
Aust. P.....	Austrian patent.
Austrl. P.....	Australian patent.
B.....	Balata.
b. p.....	Boiling point.
Can. P.....	Canadian patent.
Conc.....	Concentrated.
Coag.....	Coagulation.
dil.....	Dilute.
D. R. P.....	German patent.
E. P.....	English patent.
F. P.....	French patent.
F. M. S. Pat.....	Federated Malay States patent.
Hexa.....	Hexamethylene tetramine.
Holl. Pat.....	Holland patent.
inorg.....	Inorganic.
Jpn. P.....	Japanese patent.
m-.....	Meta.
m. p.....	Melting point.
m. w.....	Molecular weight.
org.....	Organic.
o-.....	Ortho.
p-.....	Para.
ppt.....	Precipitate.
R.....	Rubber.
S.....	Sulfur.
Sc.....	Sulfur (combined).
Sf.....	Sulfur (free).
Synth.....	Synthetic.
Temp.....	Temperature.
U. S. P.....	United States patent.
V.....	Viscosity.
Vulc.....	Vulcanization. Vulcanized.
&.....	and.



## JOURNAL ABBREVIATIONS

The journals which have actually been consulted in the preparation of this survey are shown by the volume numbers and years given in parenthesis after the full title. The figures are inclusive, e.g., (1-10) (1913-1922) indicates that the journal was covered through and including Vol. 10 (1922). Missing numbers in each volume are also given. There are many journal abbreviations in the literature for which the full title has not been found. In such cases reference is given to the Author Index where the abbreviation is located.

ABBREVIATION	FULL TITLE
Abs. Repert .....	See Chevallier (1).
Acad. Sci. Paris.....	Académie des Sciences. Paris.
Aerztl. Centr. Anz.....	See Coester (1).
Agr. Bull. F. M. S.....	Agricultural Bulletin of the Federated Malay States. Kuala-Lumpur. (1-9) (1912-1921).
Akad. Wiss. Wien.....	Akademie der Wissenschaften in Wien. See Sitz. Akad. Wiss. Wien.
Allgemeines J. ....	Allgemeines Journal der Chemie. Scherer. (1-10) (1798-1803).
Allgem. Hopfenzeit. ....	Allgemeine Brauer-und Hopfenzeitung.
Allg. Nord. Ann. Chem.....	Allgemeine Nordische Annalen der Chemie Scherer. (1-8) (1819-1822).
Ambl. Ber. ....	Ambl. Ber. über die Wiener Welt Ausstellung. Braunschweig.
Am. Chem. J.....	American Chemical Journal. (1-50) (1879-1913).
Am. Chem. Rev.....	American Chemical Review. (1-5) ( -1885).
Am. J. Pharm.....	American Journal of Pharmacy. (27) (35-94) (1863-1922).
Am. Rev. Tropical Agr.....	See Olsson-Seffer, P. (1).
Anal. Chem. ....	Zeitschrift für analytische Chemie.
Analyst .....	The Analyst. (Through 1922).
Angew. ....	Zeitschrift für angewandte Chemie. (1-35) (1887-1922).
Ann. ....	Annalen der Pharmacie. Annalen der Chemie und Pharmacie. Annalen der Chemie. (1-428) (1832-1922).
Annal. Télégr. ....	Annales Télégraphiques.
Ann. Botany .....	Annals of Botany.
Ann. Chem. Pharm. ....	See Ann.
Ann. Chim. ....	Annales de Chimie et de Physique. (1789-1921).
Ann. Chim. Anal. ....	Annales de Chimie analytique et revue de Chimie analytique.
Ann. Chim. Appl. ....	Annali di chimica applicata. (1-12) (1914-1919).
Ann. Micro. ....	Annales Micrographie.
Ann. J. Bot. ....	Annales du Jardin Botanique de Buitenzorg.

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ABBREVIATION	FULL TITLE
Ann. Physik. ....	Annalen der Physik. (1799-1818).
	Annalen der Physik und der Physikalischen Chemie. (1819-1824).
	Annalen der Physik und Chemie. (1824-1921).
Ann. Phil. ....	Annals of Philosophy. (1813-1826).
Ann. Pl. Ind. Ch. ....	See Heim & Marquis (1).
Anorg. ....	Zeitschrift für anorganische und allgemeine Chemie.
Anz. Akad. Wissen. Wien. ....	Anzeiger der Akademie der Wissenschaften in Wien.
Apoth. Zt. ....	Apotheker Zeitung. (1881-1922).
Arb. Pharm. Inst. Univ. Berlin. ....	See Lenz (1).
Arch. Expt. Path. Pharm. ....	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Pharm. ....	Archiv der Pharmazie.
Arch. Rubbercultuur ....	Archief voor de Rubbercultuur in Nederlandsch-Indië.
Armour Eng. ....	Armour Engineer.
Assoc. France ....	Association Française pour l'avancement science.
Athenæum (London) ....	See Brockedon (3).
Atti. Accad. Lincei. ....	Atti. della reale accademia dei Lincei.
Bayer. Ind. Gewerbeblatt. ....	Bayerisches Industrie-und Gewerbeblatt. (1-54NS) (1869-1922).
Ber. ....	Berichte der deutschen Chemischen Gesellschaft. (1-55) (1868-1922).
Ber. Pharm. Ges. ....	Berichte der deutschen pharmazeutischen Gesellschaft. (1-6).
Berz. Jahresb. ....	Jahresbericht über die Fortschritte der Chemie und Mineralogie. Berzelius. (1-30) (1821-1851).
Biochem. J. ....	Bio-chemical Journal. Liverpool.
Boston J. ....	Boston Journal of Chemistry and Popular Science Review. (4-17) (1869-1883).
Bot. Centr. ....	See Henri, V. (4).
Bot. Jahresber. ....	Botanischer Jahresbericht.
Brewster's J. ....	Brewster's Journal. (1824-1832).
Bull. Agr. Ceylon. ....	Bulletin of the Department of Agriculture. Ceylon.
Bull. Agr. Intelligence. ....	Bulletin of Agriculture Intelligence and Plant Diseases.
Bull. Agr. Str. F. M. S. ....	Agricultural Bulletin of the Straits and Federated Malay States. Singapore. (10) (1911).
Bull. Assoc. Planters de Caout. ....	Bull. de l'Association des Planteurs de Caoutchouc.
Bull. Caout. Inst. Col. Mar- seille ....	Bulletin des Caoutchoucs de l'Institut Colonial de Marseille.
Bull. Fed. Ind. Chim. Belg. ....	Bulletin de la Federation des Industries chimiques de Belgique.
Bull. Imp. Inst. ....	Bulletin of the Imperial Institute. (1-20) (1903-1922).
Bull. Museum d'Histoire Na- turelle ....	See Lecompte, H. (1).
Bull. de l'Office Colonial. ....	See Heim, F., & Marquis, R. (1).
Bull. R. G. A. ....	Bulletin of the Rubber Growers Association. (1-4) (1919-July, 1922).
Bull. Sci. pharmacol. ....	Bulletin des sciences pharmacologiques. Paris.

ABBREVIATION	FULL TITLE
Bull. Soc. Chim.....	Bulletin Société chimique de France. (1859-1922).
Bull. Soc. d'Encouragement...	Bulletin de la Société d'encouragement pour l'industrie nationale. (1-134) (1802-1922).
Bull. Soc. Ind. Amiens.....	Bulletin de la Société industrielle d'Amiens. (14-47) (1876-1909).
Bull. Soc. Ind. Mulhouse.....	Bulletin de la Société industrielle de Mulhouse. (26-87) (1854-1921).
Bull. Soc. Ind. Rouen.....	Bulletin de la Société industrielle de Rouen. (1-46) (1873-1920).
Bull. Soc. Pharm. Bordeaux...	Bulletin des travaux de la société de pharmacie de Bordeaux.
C. A. ....	Chemical Abstracts. (1-16) (1907-1922).
Can. Chem. J.....	{ Canadian Chemical Journal. Cont'd as Canadian Chemistry and Metallurgy. (1-6) (1917-1922).
Can. Chem. Met.....	
Caout. ....	Caoutchouc et la Gutta-percha. (1-19) (1904-1922).
Centr. ....	Chemisches Centralblatt. (1830-1922).
Centr. Bakt. ....	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten. (1921-1922).
Chandler's Am. Chem.....	Chandler's American Chemist. (1-7) (1870-1877).
Chem. Age .....	Chemical Age (New York). (1-2) (1919) ; (28-30) (1920-1922).
Chem. Age (London) .....	Chemical Age (London). (Through 1922).
Chem. Eng. (Phila.) .....	The Chemical Engineer. Cont'd as Chemical Age (New York). Through April, vol. 28, (1922).
Chem. Gaz. ....	Chemical Gazette. Cont'd as Chemical News. (1-18) (1842-1859).
Chem. Ind. ....	Die Chemische Industrie. (1-44) (1878-1920).
Chemische Rundschau .....	See Henriques, R. (5) & (6).
Chemist .....	The Chemist. (1-5) (1840-1858).
Chem. Met. Eng.....	Metallurgical and Chemical Engineering. Cont'd as Chemical and Metallurgical Engineering. (Through 1922).
Chem. News .....	Chemical News and Journal of Physical Science. Cont'd as Chemical News and Journal of Industrial Science. (1-124) (1860-1922).
Chem. Phys. Schriften.....	See Achard (1).
Chem. Rev. Fett. Harz. Ind..	Chemische Revue über die Fett-und Harz-Industrie. (9-25) (1902-1918).
Chem. Tech. Ind.....	Chemisch-Technische Industrie.
Chem. Tech. Repert.....	Chemisch-Technisches Repertorium. Supplement to Chem. Zt. (1886-1917). Missing Nos. 4, 6, 22, 78 & 106 (1908).
Chem. Tech. Repert. (Jacobson) .....	Chemisch-Technisches Repertorium. von E. Jacobson. Pub. by R. Gaertner. (1-40) (1862-1901).
Chem. Tech. Ubers.....	Chemisch-Technische Übersicht. Supplement to Chem. Zt. (1917) (1919-1922). Missing Nos. 134 & 136 (1921).
Chem. Tech. Zt.....	Allgemeine Österreichische Chemiker- und Techniker-Zeitung.



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ABBREVIATION	FULL TITLE
Chem. Trade J.....	Chemical Trade Journal and Chemical Engineer. London. (46-71) (1910-1922).
Chem. Umschau. ....	Chemische Umschau auf dem Gebiete der Fette, Oele, Wachse und Harze.
Chem. Weekblad. ....	Chemische Weekblad.
Chem. World .....	Chemical World. London. (1-3) (1912-1914).
Chem. Zeitschrift .....	Chemische Zeitschrift mit Patent Schriften Sammlung. (1-18) (1901-1919).
Chem. Zt. ....	Chemiker Zeitung. (1-46) (1877-1922).
Chim. & Ind. ....	Chimie & Industrie. (1-6) (1917-1922).
Cir. & Agr. J. Roy. Bot. Gardens .....	Circulars and Agricultural Journal of the Royal Botanic Gardens. Ceylon.
Civ. Eng. Arch. J.....	Civil engineer and architect's journal. London.
Comm. Besoeeki. Exp. Stat.....	Communications of the Besoeeki Experimental Station. (Mededeelingen van het Besoeekisch Proefstation.) Reprinted in Arch. Rubbercultuur beginning in 1917. (Part I-VII).
Comm. Central Rubber Station .....	Communications of the Central Rubber Station. Buitenzorg, Java. (Mededeelingen van het Centraal Rubberstation.) Reprinted in Arch. Rubbercultuur beginning in 1917.
Comm. Exp. Stat. Malang....	Communications of the Experimental Station. Malang. (Mededeelingen van het Proefstation Malang.) Reprinted in Arch. Rubbercultuur.
Comm. Exp. Stat. West Java..	Communications of the Experimental Station at West Java. (Mededeelingen van het Rubberproefstation West Java.) Reprinted in Arch. Rubbercultuur.
Comm. Gen. Exp. Stat. A. V. R. O. S.....	Communications General Experiment Station A. V. R. O. S. (Mededeelingen van het Algemeen Proefstation der A. V. R. O. S.) Reprinted in Arch. Rubbercultuur beginning in Dec., 1917.
Comm. Netherlands Gov't, Delft. ....	Communications of the Netherlands Government Institute for Advising the Rubber Trade and the Rubber Industry. Established at Delft.
Congres. d'Agr. Coloniale....	See Girard, E. & Rose, E.
Corps. gras. Ind.....	Same as Les Corps gras Industriels.
C. r. ....	Comptes-rendus hebdomadaires des séances de l'académie des sciences. (1-72) (1835-1922).
C. r. Soc. Biologie.....	Comptes-rendus des séances de la société de biologie.
Crell's Chem. Ann.....	Crell's Chemische Annalen. (1789-1803).
Cultuurgids. ....	See Arens, P. (1) and Zimmerman (1), p. 330.
Deutsche Ind. Zeit.....	Deutsche Industrie-Zeitung.
Dingl. Poly. J.....	Dingler's Polytechnisches Journal. (1-337) (1820-1922).
Edinburgh Phil. J.....	Edinburgh New Philosophical Journal.
Engineer .....	The Engineer (London).

ABBREVIATION	FULL TITLE
Färberei, Musterzeit. ....	Leipziger Färber- und Zeugdrucker Zeitung.
Farben-Zeitung .....	Farben-Zeitung.
Färber-Zeitung .....	Färber-Zeitung.
Gard. Bull. ....	The Gardens Bulletin. Straits Settlements. Singapore. Includes Agr. Bull. F. M. S. 3d Series.
Gazz. Chim. Ital.....	Gazzetta chimica italiana. (1-52) (1871-1922).
Genie .....	Genie industriel.
Genie Civil .....	Genie Civil.
Genussm. ....	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel sowie der Gebrauchsgegenstände. (1-42) (1898-1921).
Giorn. Chim. Ind. Appl.....	Giornale di Chimica Industriale ed Applicata. (1-4) (1919-1922).
Greiners Rubber News.....	Greiners Rubber News. (1915-1916).
Gummi, Gutta Percha und Asbest J. ....	Gummi, Gutta Percha und Asbest Journal. Dresden.
Gummi Markt. ....	Gummi Markt. (2-6) (1908-1912).
Gummi Zt. ....	Gummi Zeitung. (1-36) (1888-1922). Missing Vol. 1, Nos. 4, 5, 7, 10, 11. 2, Nos. 5, 6, 8, 9, 10, 12. 3, No. 5. 5, Nos. 4, 10. 6, Nos. 1, 13. 9, No. 21.
Helv. Chim. Acta.....	Helvetica Chimica Acta. (1-4) (1918-1921).
Hist. Acad. Roy. Sci.....	Histoire l'Académie Royal des Sciences. (1666-1790).
Ind. Blätter. (Jacobson).....	Industrie Blätter von Jacobson.
Ind. & Comm. du Caout.....	See Anon (110).
Ind. Digest.....	Industrial Digest.
Indisch Mercureur .....	De Indisch Mercureur. Amsterdam.
Industrie Chimique .....	Industrie Chimique. Paris.
Inst. ....	Institut.
Intl. Cong. Appl. Chem.....	International Congress of Applied Chemistry. Second, Fifth, Sixth, Seventh, Eighth and Twelfth (Complete).
I. R. J.....	India Rubber Journal. (1-64) (1884-1922). Missing 1, Nos. 1, 2, 3, 4, 5. 2, Nos. 9, 10, 11. 12. 3, Entire Volume. 62, No. 3.
I. R. R.....	India Rubber Review. (4-22) (1905-1922).
I. R. W.....	India Rubber World. (1-66) (1889-1922). Missing Vol. 16, Nos. 5, 6; 19, No. 1.
J. A. C. S.....	Journal of the American Chemical Society. (1-44) (1876-1922).
J. Agr. & Hort. Soc.....	Journal Agriculture and Horticultural Society. India.
J. Agr. Tropicale.....	Journal d'Agriculture Tropicale Paris. (10-13) (1910-1913).
Jahrb. Chem. ....	Jahrbuch der Chemie. Richard Meyer. (1-28) 1891-1918).
Jahrb. Chem. Phys.....	Jahrbuch der Chemie und Physik. See J. Chem. Phys. (43-69) (1825-1833).
Jahrb. der Kautschuk Ind.....	Part of Gummi-Kalender.

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ABBREVIATION	FULL TITLE
Jahresb. Agr. Chem.....	Jahresbericht über die Fortschritte auf dem Gesamtgebiete der Agriculture-chemie.
Jahresb. Chem. Tech.....	Jahresbericht über die Leistungen der Chemischen Technologie. (1-66) (1855-1920).
Jahresber. ....	Jahresbericht über die Fortschritte der Chemie und verwandter Teile anderer Wissenschaften. (1847-1921).
Jahresber. Rein. Chem.....	Jahresbericht über die Fortschritte auf dem gebiete der reinen Chemie. (1-9) (1873-1881).
J. Am. Med. Assoc.....	Journal of the American Medical Association.
J. Chem. Ind. Tokio.....	Journal of Chemical Industry. Tokio.
J. Chem. Phys.....	Journal für Chemie und Physik. (1-64) (1811-1832).
J. Chem. Phys. Min.....	Journal für die Chemie, Physik und Mineralogie. (1-42) (1806-1824). See Jahrb. Chem. Phys.
J. Chim. Med.....	Journal de Chimie Medicale. (2-7) (1856-1861).
J. Chim. Phys.....	Journal de Chimie Physique. Geneva. (1-19) (1903-1921).
J. C. S.....	Journal of the Chemical Society of London. (1-122) (1847-1922).
J. Frank. Inst.....	Journal of the Franklin Institute. (1-194) (1826-1922).
J. I. E. C.....	Journal of Industrial and Engineering Chemistry. (1-15) (1909-1922).
J. Ind. Hyg.....	Journal of Industrial Hygiene.
J. Pharm. Chim.....	Journal de Pharmacie et de Chimie. (Series 2-5).
J. Pharm. Sci.....	Journal de Pharmacie et des Sciences Accessories. (1815-1922).
J. Phys. ....	Journal der Physik. Cont'd as Neues J. Phys. (1-8) (1790-1794).
J. Polytechnique ....	See Dingl. Poly. J.
J. Roy. Inst.....	Journal of the Royal Institution of Great Britain.
J. Roy. Soc. Arts.....	Journal of the Royal Society of Arts. (1-69) (1852-1921).
J. S. C. I.....	Journal of the Society of Chemical Industry. (1-41) (1882-1922).
J. Soc. Dyers & Col.....	Journal of the Society of Dyers and Colorists.
J. Tech. Okonom. Chem.....	Journal für technische und ökonomische Chemie. Erdmann. (1-18) (1828-1833).
Kapillar Chemie .....	Kapillar Chemie.
Kolloid Chem. Beihefte.....	Kolloidchemische Beihefte. Suppl. to Kolloid Z. (1-15) (1909-1922).
Kolloid Z. ....	Kolloid Zeitschrift. (1-29) (1909-1922).
Konigl. Akad. Wissen. Berlin..	See Siemens, E. W. (2).
Kunst. ....	Kunststoffe. (1-12) (1911-1922).
Lehrb. Chem. Graham-Otto...	Lehrbuch der Chemie. Graham-Otto. (Complete).
Les Corps gras Industriels....	Corps gras industriels, journal des fabricants, d'huiles, savous, suifs, bougies, etc.
Lond. Civ. Eng. Arch. J.....	London Civil Engineering and Architectural Journal.
London Artizan .....	Artizan. London.

ABBREVIATION	FULL TITLE
London & China Express.....	See Gardner, H. C. T. (2).
London J. Arts.....	London Journal of Arts and Sciences. Newton.
Mag. Pharm. ....	Magazine für Pharmacy. (1-36) ( -1831).
Malay Agr. J.....	Malayan Agricultural Journal. Cont'd from Agr. Bull. F. M. S. (10) (1922).
Malay Tin & R. J.....	Malayan Tin and Rubber Journal. (10-11) (1921-1922).
Med. Pl. ....	Medicinal Plants. Bentley & Trimen.
Mem. Acad. Sci. Paris.....	Memoirs de l'Institut National de Sciences et Arts; Sciences, Mathematiques et Physiques. (1-14) (1795-1815).
Mentor .....	Mentor.
Mercks Repert. ....	See Lee, J. E. (1).
Mitt. konig. Tech. Versuchs...	See Holde, D. (1).
Mitt. Materialprüfungsamt....	Mitteilungen aus dem (Königlichen) Materialprüfungsamt zu Berlin. (1886) (1888) (1893) (1896-1904) (1907-1921).
Monatsh. ....	Monatshefte für Chemie und verwandte Teile anderer Wissenschaften. (1-43) (1880-1922).
Monat. Ber. Konig. Akad. Sci. Berlin .....	See Siemens, E. W. (1).
Mondes .....	Mondes Revue hebdomadaire des sciences et de leurs applications aux arts et a l'industrie.
Mon. Ind. ....	Moniteur industriel, economique, commercial financier.
Mon. Prod. Chim.....	See Breuil (1).
Mon. sci.....	Moniteur scientifique. (1875-July, 1922).
Nat. Hist. Chem. Tech. Notizen .....	Naturhistorische und chemisch-technische Notizen. (1-15) (1854-1863).
N. Br. Arch.....	See Gregory (1).
Neth. Gov't. Inst. Bull.....	Same as Comm. Netherlands Gov't. Delft.
Neues Allgemeines .....	Neues Allgemeines Journal der Chemie. Cont'd as J. Chem. Phys. Min. (1-6) (1803-1806).
Neues Jahrb. ....	Neues Jahrbuch der Chemie und Physik. See J. Chem. Phys.
Neues. Jahrb. Prakt. Chem....	See Schwerdfeger (1).
Neues J. Phys.....	Neues Journal der Physik. (1-4) (1795-1797).
N. I. Rubber tijdschrift.....	Nederlandsch-Indisch Rubber tijdschrift. (1) (1916-1917).
N. Erfind. Erfahr.....	Neueste Erfindungen und Erfahrungen. (11) (1884); (20-48) (1893-1921).
Nicholson's J. ....	Nicholson's Journal. (1-36) (1797-1813).
Oefvers. af. Kongl. Vetensk. Ak. Förhandl. ....	Öfversigt af kongl. vetenskaps-akademiens förhandlingar. Stockholm.
Oesterr. Chem. Zt.....	Oesterreichische Chemiker Zeitung. (1-28) (1898-1910); (38-40) (1920-1922).
Oesterr. Ing. Arch.....	Oesterreichischer Ingenieur und Architekten-Verein.
Pharmakol, J. ....	See MacLagan, D. (1).
Pharm. Centr. ....	Pharmaceutisches Centralblatt. (Complete). See Centr.

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ABBREVIATION	FULL TITLE
Pharm. J. ....	The Pharmaceutical Journal and Pharmacist. London. (1-54) (1841-1922).
Pharm. Weekblad .....	Pharmaceutisch Weekblad voor Nederland. (45-55) (1908-1918).
Pharm. Zeit. ....	Die Deutsche Pharmazeutische Zeitung.
Pharm. Zentralhalle .....	Pharmazeutische Zentralhalle für Deutschland.
Phila. J. Med. Sci. ....	Philadelphia Journal of Medical Science.
Philippine Agr. Rev. ....	Philippine Agricultural Review.
Phot. Korr. ....	Photographische Korrespondenz.
Photo. Arch. ....	See Swan, J. W. (1).
Physik. Zeit. ....	Physikalische Zeitschrift.
Physiol. Abs. ....	Physiological Abstracts.
Polytech. Centr. ....	Polytechnisches Centralblatt. (1-41) (1835-1875).
Polytech. Gesell. ....	Polytechnische Gesellschaft zu Berlin. (17-49) (1855-1887).
Polytech. Notizblatt .....	Polytechnisches Notizblatt für Chemiker, Gewerbetreibende, Fabrikanten und Künstler. (1-49) (1846-1894).
Prakt. Chem. ....	Journal für Praktische Chemie. (1-122) (1834-1922).
Prakt. Tech. Neuzeit. ....	Der praktische Techniker der Neuzeit auf allen Gebieten. (1-2) (1872-1873).
Primrose .....	Erste Nederlandse Tijdschrift voor Rubber.
Proc. Chem. Soc. ....	Proceedings of the Chemical Society of London.
Proc. Civil Eng. ....	See Heinzerling & Pahl. (1).
Proc. Roy. Soc. Edinburgh...	Proceedings of the Royal Society of Edinburgh.
Proc. Roy. Soc. London. ....	Proceedings of the Royal Society of London. (1-101) (1800-Sept., 1922).
Pub. N. I. Landbouw Syndi- cate .....	Pub. Nederlandsch-Indisch Syndicate.
Quart. J. Comm. Res. in Tropics .....	Quarterly Journal of Comm. Research in Tropics.
Quart. J. Sci. Lit. Arts. ....	Quarterly Journal of Sciences, Literature and Arts.
R. Age .....	Rubber Age, N. Y. City. (1-11) (1912-1922).
R. Age (London) ....	Rubber Age. London. (1-3) (1920-1922).
Rec. trav. chim. ....	Recueil des travaux chimiques des Pays-Bas. (1882-1922).
Rend. Inst. Lombardo. ....	Rendiconti reale istituto Lombardo di scienze e lettere.
Rept. Gen. Chim. ....	Répertoire général de chimie pure et appliquée. (Through 1921).
Rept. Pharm. ....	Répertoire de Pharmacie. (1-31) (1875-1919).
Rept. Tech. Lit. ....	Repertorium der Technischen Literature. (1823-1912).
Rev. Chim. Ind. ....	Revue de chimie industrielle. (1-31) (1890-1922).
Rev. Crit. Clin. Med. ....	See Sabbatani, L. (1).
Rev. d. Cult. Col. ....	See Hart (1) & Parkin, J. (6).
Rev. des Mines. ....	Revue universelle des mines, de la métallurgie.
Rev. Gen. Chim. ....	Revue générale de chimie pure et appliquée. (1-20) (1899-1917).
Rev. Ind. ....	Revue Industrielle.
Rev. Sci. Ind. ....	Revue Scientifique et Industrielle.
Riga. Ind. Zeit. ....	Rigasche Industrie Zeitung. (1-38) (1875-1913).

ABBREVIATION	FULL TITLE
Rubber Recueil .....	International Rubber Congress. Batavia. 1914. Reviewed in I. R. J. 51, 258 (1916); Gummi. Zt. 29, 533 (1915); Angew. Chem. 28, II, 248 (1915).
Russ. ....	Journal of the Russian Physical-Chemical Society.
Russki. Vrach. ....	See Mikhaylorskii, I. P. (1).
Schiek, Onderz. ....	See Oudemans.
Sci. Am. ....	Scientific American.
Science ....	Science.
Silliman's Am. J. Sci. ....	American Journal of Science and Arts. Silliman. (1819-1922).
Sitz. Akad. Wiss. Wien. ....	Sitzungsberichte Akademie der Wissenschaften in Wien. (1-129) (1848-1920).
Soc. Anciens. Elèves. ....	Société Anciens des Ecoles Nationales d'Arts et Métiers.
Soc. de Biol. de Paris. ....	See Henri, V. (4).
Soc. Chim. Belg. ....	Société chimique de Belgique. (1-30) (1887-1921).
Soc. etudes colon. ....	See Lecompte (1).
Soc. franc. de phys. ....	Société Française de Physique.
Spatula .....	Spatula.
Straits Budget .....	The Straits Budget. Singapore.
Süddeut. Apoth. Ztg. ....	Süddeutsche Apotheker-Zeitung.
Svensk Kem. Tid. ....	Svensk Kemisk Tidskrift. Stockholm. (1-33) (1889-1922).
Tech. Chem. Jahrb. ....	Technisch-Chemisches Jahrbuch. Biedermann. (1-28) (1878-1905).
Tech. Monats. ....	Technische Monatshefte, Zeitschrift für Technik, Kultur und Leben.
Text. Manuf. ....	Textile Manufacturers Journal.
Teysmannia .....	Teysmannia. (Buitenzorg).
Tropenpflanzer .....	Tropenpflanzer. (1-22) (1897-1919). Missing Vol. 1, No. 3; 2, Nos. 1, 3; 3, Nos. 7, 9, 11; 5, Nos. 1, 2; 7, No. 9, 12; 8, No. 11; 9, No. 11; 10, Nos. 2, 7; 11, Nos. 3, 5; 12, No. 9.
Tropenpflanzer Beihefte .....	Tropenpflanzer Beihefte. (11-14) (1910-1913).
Trans. Roy. Soc. ....	Transactions of the Royal Society of London. (1-222) (1665-1922).
Trop. Agr. ....	The Tropical Agriculturist. (32-34) (1909-1910).
Verein. Deut. Ing. Wochen- schrift .....	Verein Deutscher Ingenieure. Wochenschrift.
Verh. Vereins. Beförd. Ge- werbe. ....	Verhandlungen des Vereins zur Beförderung des Gewerbefleisses. (1-99) (1822-1920).
Wick's Gewerbe-Zt. ....	Wick's deutsche illustrierte Gewerbezeitung.
Wiss. Veröffentl. Siemens- Konzern .....	Wissenschaftliche Veröffentlichungen aus dem Siemens-Konzern.
Wojeuno Med. J. ....	Wojeuno medizinski journal.
Zeit. Chem. ....	Zeitschrift für Chemie. (1-14) (1858-1871). Zeitschrift für Chemie und Pharmacie. Kritische Zeitschrift für Chemie, Physik und Mathematik.

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ABBREVIATION	FULL TITLE
Zeit. Chem. Ind.....	Zeitschrift für die chemische Industrie. See Angew.
Zeit. Elektrochem. ....	Zeitschrift für Elektrochemie und angewandte physikalische Chemie. (1-28) (1894-1922).
Zeit. Oester. Apoth. Vers.....	Zeitschrift des allgemeinen Oesterreichischen Apotheker-Vereins.
Z. Öffentl. Chem.....	Zeitschrift für öffentliche Chemie. (1-27) (1893- 1921).
Z. Photochemie .....	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.
Z. Physiol. Chem.....	Zeitschrift für physiologische Chemie.

# ORGANIC ACCELERATORS OF VULCANIZATION

BY

DR. L. B. SEBRELL

The use of organic compounds in the vulcanization of rubber is one of the most important, as well as one of the most recently developed, phases of rubber chemistry. Inorganic compounds such as lime, magnesia and various lead oxides and carbonates have been known to hasten the addition of sulfur to rubber almost from the time of the discovery of the vulcanization process. Chas. Goodyear, the discoverer of vulcanization, in his early experiments had made use of white lead to reduce the time of heating and to improve the quality of the product. Its use was mentioned in his patent of 1844. Goodyear, C. (1).<sup>\*</sup> The use of ammonia as an aid in the vulcanization process was patented in 1881, Rowley, T. (1),<sup>\*</sup> but it was not until 1906, less than twenty years ago, that any organic compounds were so used. In that year it has been reported, Geer, W. C. (2),<sup>\*</sup> that aniline, and later thiocarbanilide were used as vulcanization aids. Since that time the list has been extended to include many hundreds of organic compounds of various types.

We may define an accelerator, and more especially an organic accelerator, as any compound which when added to a rubber-sulfur mix will reduce the time necessary to effect vulcanization and at the same time produce a product having increased physical properties. The chief aim in the early development of accelerators, both inorganic as well as organic, was to reduce the time of vulcanization; whereas in more recent years accelerators are chosen not only upon the ground of time saving in the vulcanization process but also on the basis of added physical properties.

It might be assumed that accelerators could properly be termed vulcanization catalysts, since they speed the reaction of sulfur and rubber, since they are used in small amounts, and also because the nature of the final reaction product of rubber and sulfur is in all probability the same whether an accelerator is present or not. It is, however, extremely doubtful whether or not they can be considered as true catalysts, for instead of remaining unchanged during vulcanization, many of them undergo pronounced reactions with sulfur, hydrogen sulfide or the metallic oxides present in the mix. Such reactions

<sup>\*</sup> All reference numbers refer to the Author Index in this volume.



tend to form active intermediate compounds from which the original accelerator cannot be regenerated. Also the physical properties of a vulcanized rubber-sulfur mixture, containing the same amount of combined sulfur, vary according as to whether the product was obtained with or without an accelerator. We should, therefore, regard these compounds, used to produce the above effects, not as true catalysts, but as limited catalysts or, as they are more commonly called, accelerators.

The mode of action by which organic accelerators increase the rate of reaction between rubber and sulfur and at the same time produce a marked change in the physical properties of the resulting vulcanisate, has been a problem confronting rubber chemists since the time of their discovery. During recent years much progress has been made but the exact mechanism of reaction is in many cases yet undetermined. It is now the general opinion, as will be shown later, that accelerators in some manner exert their effects by transforming sulfur in the inactive state into active sulfur, at the same time producing polymeric changes in the rubber. For this reason it is interesting to note, in passing, one or two theories for their action which have been proposed. Twiss, D. F. (1), suggested that the action of accelerators might be either on the natural proteins of the rubber, on the sulfur, to change it into a different form, or on the rubber hydrocarbon itself. The first he quickly discarded when it was found that the accelerators used worked equally well in rubber from which the proteins had been removed. With respect to the second, Twiss, D. F., and Thomas, F. (1), investigated the allotropic forms of sulfur and found little difference in activity between soluble and insoluble sulfur between 68° and 188° C. The third theory has not been generally developed although it has received some small amount of evidence through the work of Le Llanc, M., & Kroger, M. (1). These investigators found that the viscosity of rubber solutions decreased with increase in the dielectric constant of the solvent, and that the introduction of an accelerator also caused a further reduction in viscosity. These observations are possibly suggestive that the influence of accelerators is exerted upon the rubber and constitute the only direct evidence in favor of this view.

Before proceeding further we should ascertain the nature of the change produced by accelerators in the rate of chemical cure as compared with the change in the physical properties of the same sample. It has generally been found that the maximum physical properties of a pure gum stock, or one containing small amounts of zinc oxide, are reached at a sulfur coefficient of from three to four. Van Rossem, A. (6), has shown that although the sulfur coefficient may give an excellent indication of the quality of pure gum-sulfur mixtures, it will not give a satisfactory indication of the physical properties of an accelerated stock. Kratz, G. D., and Flower, A. H. (2),

in comparing the effects produced by an inorganic accelerator with those given by an organic accelerator in the same stock, arrived at the conclusion that "no direct relationship exists between the sulfur coefficient and the state of cure as measured by the physical properties of the mixture." They further concluded that "when mixtures are vulcanized quickly with inorganic accelerators the correct state of cure as reflected by their physical properties is obtained at abnormally low sulfur coefficients." A further study of the effect of organic accelerators upon the vulcanization coefficient and on the related physical properties has been made by Cranor, D. F. (1). He compared the results of samples vulcanized with the aid of hexamethylenetetramine and dimethylamine-dimethyldithiocarbamate with those to which no accelerator had been added. His tests showed that with a rubber-sulfur-zinc oxide mix containing no accelerator, the best cure was obtained in an hour and a half with a sulfur coefficient of 2.85. If one-half of one per cent of the dimethylamine-dimethyldithiocarbamate was added, the time of cure was reduced to four or five minutes, the ultimate tensile was increased 500 to 600 lbs. per sq. in. and the sulfur coefficient was found to be only 1.21. A similar stock containing 1 per cent of the dimethylamine derivative on storage for one month was found to be vulcanized sufficiently to give a tensile of 2000 lbs. per sq. in. and a vulcanization coefficient of 0.70. The conclusion drawn from these experiments was that the vulcanization coefficient is no measure of the best cure in the case of accelerated stocks, while good technical cures may be obtained with very low coefficients of vulcanization.

More recent has been the investigation of Shephard, N. A., and Krall, S. (2). They used hexamethylenetetramine, p-nitrosodimethylaniline, aldehyde ammonia and thiocarbanilide in a basic stock in such amounts that when all were cured for sixty minutes they gave the same physical states of cure. The vulcanization coefficients on these matched sixty minute cures were 0.87, 1.03, 0.98 and 1.38 respectively. Here again it appears that organic accelerators have a more pronounced effect upon the physical properties than upon the chemical state of cure.

O. de Vries (25), believes that organic accelerators may have a stronger accelerating effect upon the processes that alter the mechanical properties than on the combining of the rubber with sulfur. The results of further work, to be described later, tend to bear out De Vries' assumption, and to show that in the case of many organic accelerators two separate reactions are at work. The one tending to increase the rate of chemical cure or to decrease the time of cure, while the other brings about changes in the physical properties. With nearly all organic accelerators the second action is the most pronounced and is the one which is most responsible for their widespread use.

*Early Development of Organic Accelerators.*

Now that the characteristic action of organic accelerators has been briefly outlined, we may turn back and trace their development by means of the many researches which have been made from time to time as to their use and action. The first patent, Bayer & Co. (15), for the use of an organic compound as an accelerator of rubber vulcanization was granted in 1912. At that time they were seeking a way to improve the quality of synthetic rubber, and knowing that basic inorganic compounds accelerated the vulcanization of natural rubber, they selected piperidine, one of the strongest organic bases, for trial. The results were quite surprising, and were rapidly extended to other organic bases and to vulcanization of natural rubber. Since the free bases were difficult to handle, use was made of their carbon bisulfide addition products. These were found to be more active than the free bases if used in conjunction with zinc oxide. For these inventions many other patents were issued. Bayer & Co. (5), (6), (7), (9), (14), etc.

The Bayer Company has been accorded, until recently, the honor of being the first to employ organic compounds as accelerators of vulcanization. This has been so only because they were the first to file a patent application covering the use of a specific compound. Spence, D. (26) & (28), has always maintained that he had made use of the base piperidine and many other organic compounds including p-nitrosodimethylaniline prior to 1912. He did not publish specific data at the time of his discovery and for this reason has lost a considerable part of the honor that might otherwise have come to him. More recently, Geer, W. C. (2), evidence has been brought forward to show that aniline and thiocarbanilide were used in America as early as 1906 by Marks and Oenslager. We now feel fairly certain that the use of organic accelerators originated in America with Marks, Oenslager and Spence, even though priority of publication was obtained by a foreign Company.

Since the German workers found so many organic bases or their derivatives which would function as accelerators, they endeavored to cover the most important ones in a single patent, Bayer & Co. (19). This patent contains very broad claims and covers the use of all bases having a dissociation constant greater than  $1 \times 10^{-8}$ , and which show an alkaline reaction at the vulcanization temperature. The patent specifically included ammonia compounds and derivatives, both inorganic and organic, such as sodium amide, aromatic diamines, the quaternary ammonium bases, aldehyde ammonia or the products of the condensation of ammonia with aldehydes such as formaldehyde, acetaldehyde, benzaldehyde, etc. All of these compounds have, according to the patent claims, a basic reaction both at ordinary temperatures and at the temperature of vulcanization. This patent is

an exceedingly interesting one because of its scope, and the fact that it would include some of the best known accelerators.

Kratz, G. D., Flower, A. H., and Shapiro, B. J. (1), have compared the activity of several bases as accelerators to ascertain the relation between their basicity and their accelerating power. They found that the strong base phenylhydrazine with a dissociation constant of  $1.6 \times 10^{-9}$  had almost no accelerating power, in fact it was almost a negative accelerator. M-phenylenediamine, on the other hand, which had the lowest dissociation constant,  $1.35 \times 10^{-12}$ , gave the best results of any of the compounds tested. The conclusion must therefore be drawn that the activity of organic bases as accelerators is in no way proportional to their basicity as indicated by the dissociation constant. The increase in activity of a base after reaction with carbon bisulfide is well illustrated by the case of phenylhydrazine mentioned above. While the free base is a negative accelerator, its carbon bisulfide addition product has been found to be a fair accelerator.

About this time S. J. Peachey announced the discovery of the first of his nitroso accelerators (4). The first of the series, p-nitrosodimethylaniline, is now a well-known accelerator. This was the first organic compound to be used as an accelerator which possessed an acidic rather than a basic reaction. Up until this time it was generally believed that all organic compounds which would function as accelerators were nitrogen bases or a derivative of them. The list of nitroso accelerators has been extended to include the nitroso phenols, nitroso cresols (5), and nitroso benzene (16). It is also interesting to note that while p-nitrosophenol is an accelerator, p-amidophenol is without such action (8). Since basicity could no longer be regarded as a necessary adjunct to organic accelerators, attention was centered upon the nitrogen. This element had thus far been found to be a common constituent of all accelerators. Many chemists believed so thoroughly that nitrogen was the active or essential agent in accelerators, that in comparing the relative activity of several organic compounds they used amounts proportional to their nitrogen content. This theory was also discarded when Ostromuiskenski, I. (13), found that zinc alkyl xanthates formed by action of carbon bisulfide on alcohols in the presence of alkali were good accelerators. These compounds are not basic in reaction, neither do they contain any nitrogen. Zinc thiophenol has also recently been added to the list of non-nitrogenous accelerators, Bedford, C. W., & Sebrell, L. B. (1). These two classes of compounds will be more fully discussed later. It is evident, from the data given above, that the mechanism of the action of organic accelerators is a much more complex problem than it was first thought.

Before turning to the theories which have been proposed from time to time to explain the mechanism of the action of accelerators,

we should first review the results obtained in several of the researches made upon the nature and properties of the compounds themselves.

Twiss, D. F., & Brazier, S. A. (1), studied the increase in the rate of vulcanization when increasing amounts of aldehyde ammonia were used as an accelerator. They found that the addition of  $\frac{1}{8}$ ,  $\frac{1}{4}$ ,  $\frac{1}{2}$  and 1 per cent of the accelerator increased the rates of vulcanization 1.7, 3, 5 and 7.5 times the normal. They also found that aldehyde ammonia would function as an accelerator at as low a temperature as  $98^{\circ}$  C.

This work was then extended by Twiss, D. F., & Howson, C. W. (1), to include the action of several accelerators in the presence of zinc oxide. It was generally known that thiocarbanilide functioned as an accelerator only in the presence of zinc oxide. Twiss thought that this might be suggestive of the mechanism of its action, the active substance being carbodiphenylimide, formed by the desulfurizing action of zinc oxide. A trial showed that the carbodiphenylimide was not active, due perhaps to its tendency to polymerize. Neither was the nascent compound, supposedly formed in the rubber by the action of mercuric oxide, any more active.

The addition of a small amount of zinc oxide, 1 per cent, to a hexamethylenetetramine stock was found to greatly improve the rate of cure. It was noticed, however, in this case that in plotting the results of a long series of cures the tensile attained a maximum value, then fell rapidly for a time, after which it began to increase again. The normal action of zinc oxide in an unaccelerated stock is to reduce the elongation at a certain cure and to give a slight stiffening action, but the effect is not comparable with that obtained in a stock containing both zinc oxide and an accelerator. Twiss repeated the experiment with hexamethylenetetramine and small amounts of zinc oxide several times, but always obtained the same  $\sim$  shaped curve. With other accelerators and 1 per cent of zinc oxide, this decreasing and increasing tensile effect with the corresponding effect upon the elongation was not noted. Triphenylguanidine with 1 per cent of zinc oxide gave practically the same rate of cure as the pure gum stock, the only noticeable effect being upon the elongation which decreased rapidly. Stocks containing aldehyde ammonia as an accelerator were found to give good cures at temperatures as low as  $98^{\circ}$  C. The addition of 1 per cent of zinc oxide produced no marked effects other than a slight stiffening action similar to that obtained with triphenylguanidine.

Twiss ventured the opinion that the inflection in the case of the last two named accelerators might take place at a "stage of vulcanization much beyond the range of convenient testing." It is worthy of note that the inflection in the tensile curve of hexamethylenetetramine with 1 per cent of zinc oxide takes place while sulfur is constantly being added to the rubber. There is no downward dip or

break in the curve for the addition of sulfur. This change must therefore take place independently of the rate of addition of sulfur and is most probably concerned with the physical state of the rubber. The break in the tensile curve occurs at a sulfur coefficient of from 4 to 5 which represents approximately the combined sulfur value of the so-called optimum cure. At this time Twiss was somewhat undecided as to the probable cause of the above action of hexamethylenetetramine when used with small amounts of zinc oxide. He thought that it probably indicated that two distinct processes were at work causing the change in the physical properties of the rubber, the point of inflection representing the stage at which the one became inactive and was succeeded by the second.

Not being content with the above explanation, Twiss, D. F. (12), continued his work further. He studied the action of this accelerator when used not only with 1 per cent of zinc oxide but with 2 per cent and 5 per cent as well. With the 2 per cent or 5 per cent of zinc oxide the break, above referred to, was not found, a smoothly increasing curve being obtained. All the work up until this time had been done on a base mix containing 90 per cent of rubber and 10 per cent of sulfur with 1 per cent of the accelerator. To make sure that the above effect was not a result of the particular sulfur ratio chosen, experiments were made using lower amounts of sulfur. In all cases the break was only obtained when 1 per cent of zinc oxide was used and the range of vulcanization sufficiently extended. In this work further attention has been given to the cause of this discontinuity in the tensile curve. It has now been shown that the effect appears while sulfur is being constantly added to the rubber, and that it does not appear when more than 1 per cent of zinc oxide is used. Twiss therefore concluded that it is due to depolymerization of the rubber caused, not by the hexamethylenetetramine itself, but by some decomposition product of it. It does not occur when more than 1 per cent of zinc oxide is used for one of two reasons, either the formation of the direct accelerator is favored by the use of excess zinc oxide, less of the accelerator decomposing to cause the depolymerization, or the decomposition product of the accelerator is acidic and the excess of the oxide is necessary to neutralize it. It is probable that the first reason is more nearly correct but it is difficult to give absolute proof. It is generally known, however, that with accelerators which require the presence of zinc oxide for activation, as nearly all do, that 1 per cent is in most cases insufficient to produce the best results. Most accelerators require the presence of at least 3 per cent of zinc oxide for the attainment of their maximum effect.

Kratz, G. D., Flower, A. H., & Shapiro, B. J. (2), have studied the relative accelerating power of aniline and diphenylthiourea, both in pure gum mixtures and in the presence of zinc oxide. In the

absence of zinc oxide it was found that the accelerating power of aniline was much greater than a molecularly equivalent quantity of diphenylthiourea. The same maximum tensiles were obtained with aniline either with or without zinc oxide but the highest coefficient of vulcanization was found when zinc oxide was absent. The rate of cure of diphenylthiourea in the presence of zinc oxide is much faster than that of aniline, although finally both give the same maximum tensiles and at about equal sulfur coefficients. These investigators also noticed that zinc oxide had less effect when used with aniline than when used in conjunction with the diphenylthiourea in the same formula. With aniline it seemed to exert a physical effect only, causing a stiffening action to take place. The difference between the tensile curves for aniline with and without zinc oxide also showed much less difference than did those for diphenylthiourea under like conditions. The same thing is true for the curves showing the vulcanization coefficients. In fact, diphenylthiourea, without zinc oxide, gives the same rate of cure with only slightly better tensiles than does the unaccelerated pure gum stock. When zinc oxide was added to the stock containing diphenylthiourea a marked increase in activity was at once noted. Short cures gave products of high tensile strength and low combined sulfur.

Kratz and his coworkers were of the opinion that in the case of diphenylthiourea the function of the zinc oxide was either to facilitate the decomposition of the thiourea into a more active compound, or to combine with the decomposition products to give a zinc salt. This zinc salt being the active accelerator would probably account for the increase in rate of cure, tensiles and sulfur coefficient obtained when zinc oxide was used.

From these facts and assumptions it would appear that the action of these two compounds as accelerators is entirely different. On the one hand with diphenylthiourea the formation of an acid substance, probably a thiocarbamic acid, capable of reacting with zinc oxide is assumed, while with aniline the authors could find no evidence of the formation of an analogous salt.

Twiss (*loc. cit.*) has expressed the opinion that the acidic substance, formed by the decomposition of diphenylthiourea, which reacts with zinc oxide as mentioned above, might be phenylisothiocyanate. Accordingly, he tried compounding this acidic compound into rubber both with and without zinc oxide. He noted considerable increase in tensile on the addition of zinc oxide but neither of the tests made gave results equivalent to diphenylthiourea.

About the same time it was found that the sulfur reaction products of certain accelerators had greater curing power than the original compound. A British patent and a later U. S. patent, Bedford, C. W. (1), describe the results obtained with the sulfur reaction products of thiocarbamilide, triphenylguanidine and several other com-

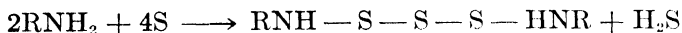
mon accelerators. The increased curing power of the thiocarbanilide-sulfur reaction product was found to be due in part to the formation of a very active compound, namely, 1-mercaptobenzothiazole, which was isolated from it, Bedford, C. W., & Sebrell, L. B. (1), (2). This compound and its reactions will be described more fully later. Bedford, C. W. & Scott, W. (1) have also shown that anhydro-formaldehyde aniline and methylenediphenyldiamine will react with sulfur to give thiocarbanilide and other thiourea derivatives. The theory has been expressed in the above researches that some or all accelerators undergo a reaction with sulfur to form the true or active accelerators. This seemed to be justified by the increased curing power of many of the sulfur reaction products. The above fact may be said to be the starting point of practically all the recent theories for the action of accelerators. It is true that our best accepted explanation of the action of organic accelerators also involves the possibility of reaction with hydrogen sulfide and metallic oxides, as well as with sulfur, but the direct sulfur reaction product was the fundamental fact from which later ones have been developed.

*Development of Theories to Account for the Mechanism of Action of Organic Compounds as Accelerators.*

We may now briefly review the various theories which have been proposed from time to time in an effort to explain the mechanism of the action of organic accelerators.

Erdmann, H. (1), as early as 1908 proposed the first theory of the action of accelerators, a theory which has been extended and modified by many later investigators.

The first serious attempt to explain the mechanism of the action of organic accelerators was made by Ostromuiskenskii, I. (15), (18), in 1916. He assumed that in the case of organic amines used in connection with metallic oxides the action was essentially a case of double catalysis. The oxide first catalyzing the amine and causing it to activate sulfur by converting it into  $S_8$ , with which the amine unites to form an unstable trithioozonide as follows:



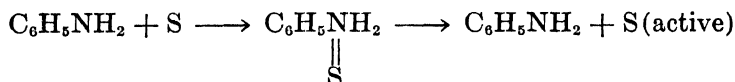
The amine then acts as an accelerator, giving up sulfur to the rubber from the above unstable compound, either by a reversal of the above reaction or by changing it to  $RNH-NHR$ . The result being the same in both cases, namely, that the amine can again take up S, thus making the process continuous.

It will be seen that the formation of the aminethioozonides is conditioned upon hydrogen being attached to nitrogen which would preclude the application of this theory to the tertiary amines. Scott, W. & Bedford, C. W. (1) have cited this as being against the



general application of the entire theory, as well as the fact that it is limited to amines which react with sulfur at the curing temperatures. This objection has been further justified since it has been found that tertiary amyl amine, U. S. P. 1,436,894, is a very efficient accelerator.

Kratz, G. D., Flower, A. H. & Coolidge, C. (1), have proposed a theory by which compounds containing nitrogen, or more especially, an active group such as an amine group, are supposed to act as accelerators. In this theory the valence of the nitrogen atom is assumed to change from three to five with the temporary addition of sulfur. This sulfur addition product then gives up its sulfur to the rubber, and reforms the original compound, which is again ready to activate more sulfur. These changes are illustrated by the following equation:



The increased curing power of p-phenylenediamine over that of aniline was found to be in accord with the above theory for the following reason: Phenylenediamine,  $(\text{NH}_2\text{C}_6\text{H}_4\text{NH}_2)$ , with two active  $\text{NH}_2$  groups to serve as points of activation of sulfur should be twice as powerful as a corresponding molecular fraction of aniline. This the above authors found to be the case, and therefore felt that their beliefs as to the mechanism of nitrogen compounds had been confirmed.

Another, and somewhat fanciful, explanation of the action of organic accelerators in the vulcanization process has been given by Dubosc, A. (30). He assumes that organic accelerators undergo reaction with sulfur to form sulphocyanic acid which he considers to be the active agent. It functions by giving up sulfur to the rubber, forming hydrocyanic acid. This in turn by further action of the sulfur regenerates the sulphocyanic acid. These reactions may be represented in the case of aniline as follows:

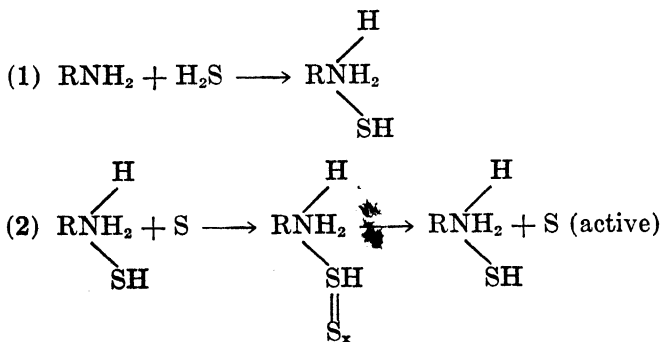


The above reaction whereby aniline on reaction with sulfur produces acetylene and sulphocyanic acid is open to considerable question. No one else has ever reported such products as obtained from this reaction and it is not reasonable to suppose that the reaction would take place differently in rubber. The writer has, however, been able to identify sulphocyanic acid among the sulfur reaction products of hexamethylenetetramine.

Dubosc describes sulfofocyanic acid as a condensator, ascribing to it the property possessed by organic accelerators of changing the physical properties of the rubber. Activation of sulfur may also be

accomplished, according to Dubosc, by the interaction of sulfur dioxide and hydrogen sulfide. The sulfur dioxide being formed from the action of metallic oxides and sulfur, and the hydrogen sulfide by the action of the resins and proteins with sulfur. This action is also somewhat questionable, since it is doubtful if the two gases would be formed in the exact proportions required. This explanation did, however, precede the publication of a patent by Peachey, S. J. (14), in which vulcanization of rubber was effected by treatment of the rubber with the above two gases. There is a class of organic accelerators, of which *p*-nitrosodimethylaniline is an example, which are known to liberate both hydrogen sulfide and sulfur dioxide when heated with sulfur, but the majority of organic accelerators do not undergo any such reactions. Dubosc's idea that separate reactions are responsible for the increase in rate of cure and the change in physical properties, is entirely possible.

Probably the best and most generally accepted theory of the action of organic accelerators is the hydrogen sulfidepolysulfide theory or as it is now more commonly called, the polysulfide theory. This theory was originally proposed by Scott, W. and Bedford, C. W. (1) and has since been extended by others as will be discussed later. The mechanism of the action of amines as accelerators, according to this theory, consists first in the addition of hydrogen sulfide to the amino group, the valence of the nitrogen thereby being changed from three to five. The addition product, which is an ammonium sulfide derivative, is next assumed to add sulfur to form a polysulfide in a manner exactly analogous to the formation of ammonium polysulfide. This polysulfide sulfur is then easily split off in an active form for addition to the rubber. The above reactions may be represented graphically by the following equations:



The formation of the hydrogen sulfide addition product of amines may be readily illustrated by the reaction of dimethylamine and hydrogen sulfide. The amine rapidly absorbs the gas and, if sulfur

is added, a deep red color characteristic of polysulfide solutions is formed.

That polysulfide sulfur is especially active and available for vulcanization has been shown by several investigators. Bloch, I. (1), found that the hydrogen polysulfides,  $H_2S_2$  and  $H_2S_8$ , will cure rubber at ordinary temperatures, although Bruni, G. and Romani, E. (1) state that they have been unable to verify Bloch's work. Gerard, A. (1) found that concentrated solutions of alkali polysulfides would effect vulcanization, while Twiss, D. F. (12), has found that his solution of sodium hydroxide in glycerol was just as effective as an accelerator if transformed to the hydrosulfide.

Bedford and Sebrell (*loc. cit.*) have also succeeded in preparing trithio-ozone, a polysulfide form of sulfur, sufficiently active to vulcanize rubber at ordinary temperatures. These facts would tend to show that the assumptions made in the foregoing theory are fully justified.

Scott and Bedford (*loc. cit.*) have classified accelerators into two main groups according to their structure, since it was well known that all accelerators did not function in the same manner as the amines. This classification may be briefly stated as follows:

*Class I—Hydrogen-sulfide Polysulfide Accelerators.*

To this class belong all organic bases or compounds that form bases during vulcanization. These are believed to form polysulfides by reaction with hydrogen sulfide and sulfur.

*Class II—Carbo-sulphydryl Polysulfide Accelerators.*

This class includes all accelerators that contain the grouping  $\equiv C-SH$  such as the thioureas, dithiocarbamates, thiurams, mercaptans or the disulfides which may be formed from them by oxidation or reaction with sulfur.

It is to be noted that in Class I the sulhydryl group is attached to a nitrogen atom, while in Class II it is attached to carbon.

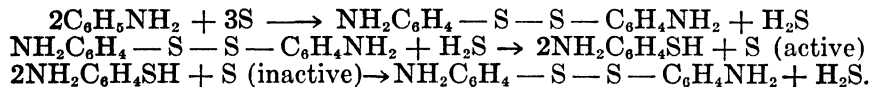
Bruni (*loc. cit.*) has proposed a classification of accelerators which is essentially the same as that given above, but he has added a third class, to include the aromatic nitroso derivatives which cannot be placed in either of the two groups mentioned above. He has also proposed a theory for the action of accelerators of Class II, a discussion of which will be given later.

It now becomes necessary, since we have before us a very broad classification of accelerators, to enumerate various members of each group and to discuss their particular action as accelerators.

The first group given above contains such well-known accelerators as the amines, aldehyde ammonia, hexamethylenetetramine, p-phenylenediamine, ethylidene aniline, anhydroformaldehydeaniline, methyl-

enediphenyldiamine, and the di- and tri-substituted guanidines. As to the specific reactions which these compounds undergo when used as accelerators of vulcanization, little information is at hand and the need of more careful research as to their mechanism is plainly evident.

We have already noted three explanations for the action of amines but thus far we have been unable to absolutely prove that any one is correct. Recently another explanation as to the action of aniline has been set forth by Kimishima, T. (1), a Japanese chemist. He assumes that aniline will react with sulfur to give dithioaniline and hydrogensulfide. The hydrogensulfide then acts on the dithioaniline to reduce it to aminothiophenol with the separation of free and active sulfur. The aminothiophenol by oxidation with sulfur again forms the dithioaniline and hydrogen sulfide which repeat the cycle. These reactions may be illustrated as follows:



Examples are given in which several samples of 92.5 parts of rubber and 7.5 parts of sulfur were heated with dithioaniline, thioaniline and aniline both in an atmosphere of air and in an atmosphere of hydrogen sulfide. It is claimed that vulcanization with the thioanilines took place only in an atmosphere of hydrogen sulfide and that in air they were apparently negative accelerators. It would seem that this alone would tend to cast some doubt upon the scheme as correctly representing the action of aniline. It has been shown, J. I. E. C. 15, 720 (1923), that rubber and sulfur alone generate considerable amounts of hydrogen sulfide which should be sufficient to reduce the dithioaniline and set free active sulfur even in the absence of an atmosphere of hydrogen sulfide. Until this theory has been more thoroughly investigated, we cannot place any confidence in it. It is also not of general application as it cannot be used to explain the action of secondary and tertiary amines.

Aldehyde ammonia, hexamethylenetetramine and p-phenylenediamine are accelerators, which, according to Scott and Bedford (*loc. cit.*), probably function because of their reaction with sulfur to form ammonia and hydrogen sulfide. These then combine with the addition of sulfur to give ammonium polysulfide, which may then give up active sulfur available for vulcanization. This explanation does not account for the increased activity of some of these accelerators in the presence of zinc oxide. It will be recalled that Twiss, D. F. & Brasier, S. A. (1), also Twiss, D. F. & Howson, C. W. H. (1), have shown that amounts of zinc oxide in excess of 1 per cent exert a pronounced effect on the action of hexamethylenetetramine and a much

less effect upon the action of aldehyde ammonia. They have also questioned the assumption that an accelerator like aldehyde ammonia reacts with sulfur in order to form the active constituent. They found that the above compound would cure at as low a temperature as 98° C. and stated that since this is the case it would seem unnecessary to assume a reaction with sulfur in order to form a more active compound. It was later shown by Bedford and Sebrell (*loc. cit.*), that aldehyde ammonia would react with sulfur at a temperature as low as 80° C., so that the above objection cannot stand.

Scott and Bedford at the time they made the above classification thought that with hydrogen sulfide-polysulfide accelerators, inorganic oxides functioned only as aids to the organic polysulfide by breaking them up into colloidal sulfur and the original nitrogen base. It would seem from the evidence, now at hand, that the action of the metallic oxides is not so simple as that just given and no doubt a better explanation will soon be put forth.

Another general class of accelerators of the hydrogen sulfide-polysulfide type are the amine-aldehyde condensation products. This class embodies such well-known accelerators as anhydroformaldehyde aniline, methylenediphenyldiamine, ethyldeneaniline in its various forms, heptaldehydeaniline and many others. All of these compounds are thought to react through the aid of hydrogen sulfide or sulfur to give polysulfides. With the exception of the research of Bedford and Scott, previously noted, on the action of sulfur on anhydroformaldehyde aniline and methylenediphenyldiamine, in which it was found that thiocarbanilide was the chief product, no further study has been made of the action of these various compounds as accelerators.

The guanidine derivatives constitute a group of compounds which must also be classed as hydrogen sulfide-polysulfide accelerators. One of the simplest compounds, aminoguanidine, was used by Twiss, D. F. (1), in 1916. The more common di- and tri-substituted guanidines are now among the more common accelerators. Kratz, G. D. Flower, A. H. and Shapiro, B. J. (*loc. cit.*), have compared the relative curing power of the monophenyl-, diphenyl- and triphenylguanidines and found that the monophenyl and diphenylguanidines were equal in curing power and that they were approximately six to seven times as powerful as the triphenylguanidine. Scott, W., J. I. E. C. 15, 289 (1923), has also determined the relative activity of several di-substituted guanidines and found them to be in the following order: di-p-tolyl, di-o-tolyl and diphenylguanidine.

The mechanism by which the guanidine derivatives accelerate vulcanization is a very interesting as well as a perplexing question. It is quite well known that all of them require the presence of zinc oxide in order to exert their maximum effect. In the early consideration of the mechanism of reaction of the disubstituted guanidines Scott and Bedford (*loc. cit.*) stated that diphenylguanidine was de-

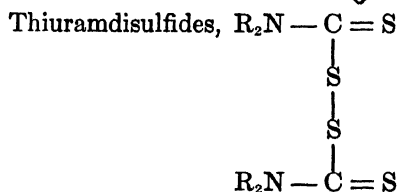
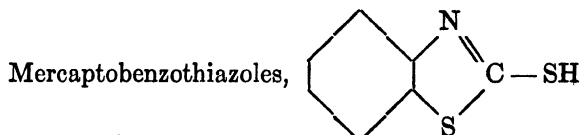
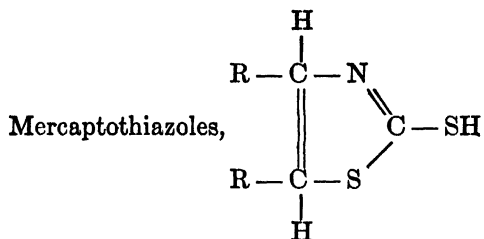
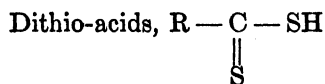
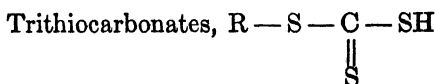
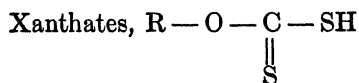
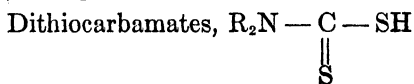
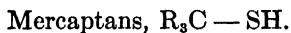
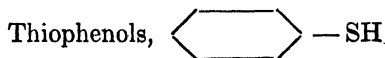
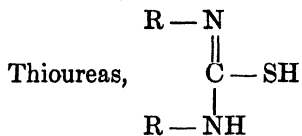
composed by the action of hydrogen sulfide to thiocarbanilide and ammonia. The various reactions which diphenylguanidine may undergo have been investigated by Bedford and Sebrell and later by Scott. The first workers found that hydrogen sulfide would react with diphenylguanidine to give an additional product which was thought to be the hydrosulfide but it could not be isolated as such. They further found that aniline and carbon bisulfide would react with diphenylguanidine to give a stable addition product, and that diphenylguanidine would react with mercaptans to give salts. Scott has carried the chemistry of diphenylguanidine further and found that diphenylguanidine would react with hydrogen sulfide and carbon bisulfide to give diphenylguanidine trithiocarbonate, a comparatively stable compound, melting at about 88-89° C. He did not submit any analytical results in support of the formula and it therefore cannot be considered as being absolutely correct, although it was found to yield trithiocarbonic acid on treatment with hydrochloric acid in the cold. With carbodiphenylimide, diphenylguanidine forms the base tetraphenylbi-guanid. Scott also made a more careful study of the reaction product of aniline, carbon bisulfide and diphenylguanidine and found it to be the diphenylguanidine salt of phenyldithiocarbamic acid.

It has already been noted that diphenylguanidine had been supposed to function as an accelerator through its decomposition by hydrogen sulfide into thiocarbanilide and ammonia. It was later shown, as described above, that hydrogen sulfide will react with diphenylguanidine not to decompose it, but to form an addition product. In view of this fact Scott then assumes that the mechanism of its action is that of a hydrosulfide accelerator similar to aniline. He reasons that it cannot be due to its decomposition products since di-*o*-tolylguanidine is more powerful and has a higher melting point than diphenylguanidine.

Scott has also investigated the action of varying amounts of zinc oxide when used in connection with the disubstituted guanidines and concluded that the remarkable increase in physical properties noted must be due to a physico-chemical action, the zinc oxide probably reacting to form derivatives corresponding to the complex zinc-ammonia compounds, zincates and thio-zincates. This assumption has not yet been verified but all present data seem to indicate that zinc oxide plays a most important part in the curing action of disubstituted guanidines.

The second group of accelerators in the polysulfide classification given above were designated as carbosulphydryl accelerators. They either contain the group  $\equiv\text{C}-\text{SH}$  or undergo reactions which tend to produce the group. It would probably be well to represent graphically the structure of the various types of accelerators in this group and to call attention to some of their general characteristics before proceeding with a more detailed discussion.

These may be represented as follows:

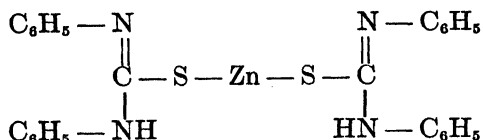


In the above formulas R has been used to represent hydrogen, an alkyl or other grouping. It will be observed that three of these general classes contain no nitrogen and it is known that at least two of them are very powerful.

All of these compounds have been found to react either directly or indirectly with metallic oxides to give metallic salts. Bedford and Sebrell have assumed that these metallic salts are the active compounds which are responsible for the activation of sulfur and the increase in physical properties. In many cases it has been found that the addition of a free amine to the zinc salt of the accelerator increases its activity. One explanation which has been offered is that the amine forms an addition product with the zinc salt which facilitates the formation of polysulfides.

The chemistry of the carbosulphydryl accelerators and their mechanism in the vulcanization process has received much more attention from research workers than have those of the hydrogen sulfide-polysulfide group. The researches made on each class of compounds, in the first of the above mentioned groups, are very interesting and a further description of them should be well in order. Bruni's theory for the action of organic accelerators will also be presented after a more complete survey of the evidence upon which it was founded.

The work of Kratz and of Twiss on the action of thiocarbanilide as an accelerator has been previously outlined. It was found that their results could not satisfactorily explain the action of this compound, although Kratz stated that it was probable that it reacted with zinc oxide to form a salt which was the active agent. The proof that such an active metallic salt is formed has been obtained by later workers. In the course of this work it was found that if aniline was added to a zinc oxide cement containing thiocarbanilide, then an air cure was obtained. It was further observed that appreciable amounts of zinc oxide were dissolved by a solution of thiocarbanilide in benzene and aniline, and that this solubility was only observed when the thiourea was present. It was therefore concluded that the air curing of the cement was due to the formation of a zinc salt of the following formula:



This salt is probably also formed during hot vulcanization and is the active curing agent forming polysulfides with additional sulfur. In support of this view the following experiment may be cited. Thiocarbanilide dissolved in benzene was cooled to 15-20° C. and litharge added with stirring. Rapid stirring for a short time produces a deep



red mercaptide which is soluble in benzene and may be separated by filtration. Slight warming precipitated lead sulfide. The addition of sulfur to the cold solution of the lead mercaptide caused a deepening of the red color. From these experiments it was concluded that the mechanism of the action of thiocarbanilide is through the formation of a metallic salt, which is then able to activate sulfur by the formation of a polysulfide. The metallic salt or polysulfide may be decomposed by hydrogen sulfide into the mercaptan and metallic sulfide, but it can be quickly reformed by an excess of the metal oxide. These reactions classify the disubstituted thioureas as carbosulphydryl accelerators, and indicate the mechanism given above.

Two other classes of accelerators, whose mechanism has been widely studied, are the dithiocarbamates, and their oxidation products, the thiuram disulfides. Both of these classes contain compounds which are perhaps as powerful as any of the known accelerators. Some members of the series were described by Bayer & Co. (6), as early as 1912 and are therefore among the oldest of our organic accelerators. It was early recognized by Ostromiuislenskii, I. (13), that the dithiocarbamates gave much better results if they were used in conjunction with some metallic oxide. The first work done on the mechanism of the action of the dithiocarbamates as accelerators was by Maximoff and by Bruni. Maximoff, A. (1), gives an account of work supposedly done in Russia during the years 1914-16, but Bruni, as will be shown later, gained priority in publication.

Maximoff undertook to determine the nature of the reaction between dithiocarbamate accelerators with zinc and lead oxides. He assumed that the increased activity noted was due most probably to the formation of compounds by the reaction of the accelerator with sulfur or with the metallic oxides, or with both. To prove this assumption he fused 5 grams of the dimethylamine salt of dimethyldithiocarbamic acid with 10 grams of sulfur and 15 grams of rubber. The resulting product was added in small amount to a rubber-sulfur mix and a fairly rapid vulcanization was obtained.

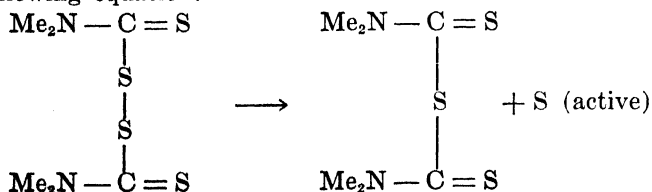
By an examination of his fusion product he was able to isolate two products in addition to the unchanged dithiocarbamate. These melted at 127° C. and 242° C. respectively. The first of these products caused rapid accelerating action, while the second had marked curing power even in the absence of metallic oxides. This latter compound was undoubtedly the zinc salt of the dithiocarbamic acid. He also investigated the composition of a sample of crude dimethylamine-dimethyldithiocarbamate and found it to consist of two additional products, one being tetramethylthiuramdisulfide, the oxidation product of the dithiocarbamate, and the other tetramethylthiourea. The tetramethylthiuramdisulfide was found to be somewhat easily decomposed into free sulfur and the monosulfide, but Maximoff was not able to cause the disulfide to vulcanize without the presence

of extra sulfur, even though he used as much as 20 per cent. The zinc and lead salts of the above dithiocarbamate were more powerful than the free base if both were used in the presence of zinc oxide. When the zinc oxide was not used or was replaced by the oxides of magnesium, calcium or barium, the curing power of the compound was greatly reduced.

The fact that the zinc and lead salts of the above dithiocarbamic acid did not cure well except in the presence of an excess of zinc or lead oxides was thought to be due to the acidity of the resins. Maximoff was of the opinion that zinc oxide by neutralizing the resin acids allowed the accelerating action to proceed to best advantage. In conclusion we may say that perhaps the most interesting and acceptable part of the work by Maximoff is his study of the composition of dimethylamine-dimethyldithiocarbamate. The work on the preparation and properties of the metallic salts of the above dithiocarbamate cannot be given preference over the earlier published data of Bruni, even though the work was supposedly done several years before it was published.

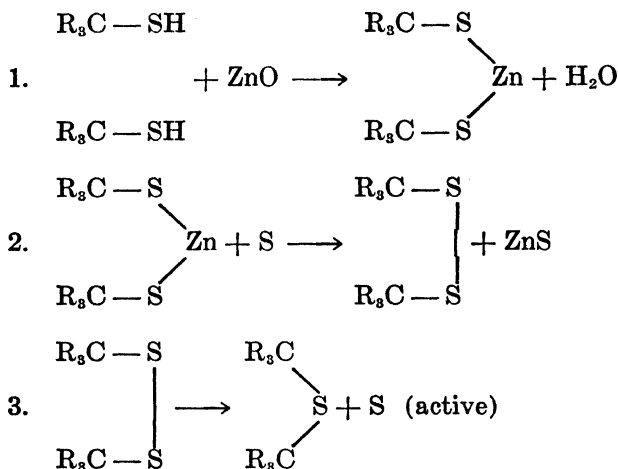
Bruni, G. (1), as early as 1920, recognized the superior curing power of the metallic salts of the dithiocarbamates and at once began a study of their reactions. He further found (3), that if an aromatic amine, such as aniline, was incorporated into a rubber-sulfur-zinc oxide mixture and the mass exposed to the vapors of carbon bisulfide that vulcanization was accomplished very quickly even at temperatures much lower than those ordinarily used. This was attributed to the formation within the rubber of thiocarbamide in an active form. It is more probable in the light of our subsequent knowledge that the rapid vulcanization was due to the formation of the zinc salt of phenyldithiocarbamic acid.

We now come to the evidence which, in Bruni's estimation, was of such great value in explaining the mechanism of acceleration of dithiocarbamates and their related compounds that he has used it as the basis for his general theory. Romani, E. (1) had found that cyclopentamethylene disulfide, obtained from the corresponding dithiocarbamate by oxidation, would vulcanize a rubber-zinc oxide mixture in the absence of any free sulfur, and that other thiuram disulfides would act in a similar manner. The curing power of tetramethylthiuramdisulfide without extra sulfur may be represented by the following equation:



This fact was regarded by Bruni as the key to the mechanism of the action of all accelerators of this type. It has been further stated by these workers that thiuramdisulfides are also formed by the action of free sulfur upon the metallic dithiocarbamates.

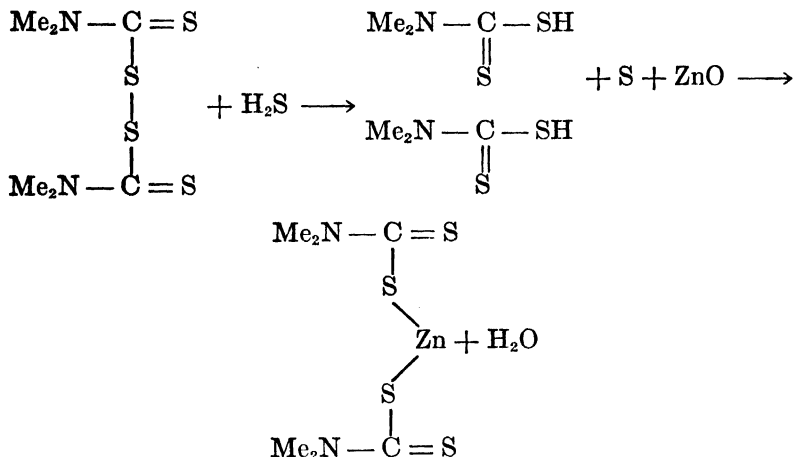
In view of the above reactions these workers have evolved a theory for the action of all accelerators of the carbosulphydryl group. This theory may best be presented by means of the following general equations.



It seemed to Bruni that compounds like the disulfides which were powerful enough to cause vulcanization by means of their own sulfur, when no other free sulfur was present, must be the active compounds which are responsible for the curing action of this type of accelerators.

This view has met with considerable criticism, the most important being through the results obtained by Bedford and his coworkers on the reactions of these compounds. In this work it was found that while tetramethylthiuramdisulfide would cure without the presence of free sulfur, it would also cure equally well without zinc oxide. The coefficient of vulcanization was the same for a 45-minute cure as for a 10 minute cure. The acetone insoluble sulfur was the same either with or without the zinc oxide and corresponded very closely to one out of four sulfur atoms in the disulfide. This, in a way, constituted a verification of the correctness of Bruni's theory. However, it could not be taken as representing the mechanism of this compound as an accelerator when used with extra sulfur, because it was known that best results are to be obtained only when zinc oxide is present. If it did represent the real mechanism, then we should expect equal results even in the absence of zinc oxide.

Further work has shown that tetramethylthiuramdisulfide will not air cure a rubber-sulfur cement either with or without zinc oxide. However, if the zinc oxide cement was treated with a small amount of hydrogen sulfide it would then air cure on standing over night. It has been recorded in the literature (Weyl—"Methodender organischen Chemie," p. 243), that aromatic disulfides may be easily reduced to mercaptans by the action of hydrogen sulfide or alcoholic potassium sulfide. The assumption was then made that hydrogen sulfide acted in a similar way upon tetramethylthiuramdisulfide reducing it to the dithiocarbamic acid with the liberation of sulfur. The dithiocarbamic acid liberated would then react with the zinc oxide to form the zinc salt which was known to be a rapid curing agent at ordinary temperatures only in the presence of excess zinc oxide.



This theory is strengthened by the fact that the above disulfide in the absence of zinc oxide will not air cure a cement even though hydrogen sulfide is present. It would seem, therefore, that the mechanism of the accelerating action of disulfides and dithiocarbamates was not through the disulfide directly, but that a polysulfide of the metallic dithiocarbamate must be the active agent. This would also account for the greater activity as accelerators of the metallic salts of the dithiocarbamates.

Bruni assumed in his theory that metallic dithiocarbamates would react with sulfur to produce the corresponding thiuram disulfides. Bedford and Sebrell (*loc. cit.*) studied the reaction of zinc dimethyldithiocarbamate with sulfur in boiling xylol, but were unable to verify the statement that any disulfide was formed. They did, however, observe that hydrogen sulfide would decompose a solution of the zinc salt of dimethyldithiocarbamic acid, with the formation of

zinc sulfide. It was further noted that if aniline was added to a zinc oxide cement containing the above zinc salt, it gave a much quicker vulcanization at room temperature than if no aniline had been added. At this time the increased effect caused by the addition of aniline was attributed to its solvent action on the zinc salt. The same phenomena have been investigated by Cadwell, S. M. (4), (5), (6), and (7), who used aniline and other aromatic amines to hasten the low temperature vulcanization of several accelerators, such as the metallic xanthates and their disulfides as well as the dithiocarbamates and the thiuram disulfides.

From the above accounts of the researches which have been made on dithiocarbamates and their corresponding disulfides we may briefly summarize the two opposing theories which have been set forth to explain their action.

Bruni, by reason of the fact that the metallic dithiocarbamates will not cure without extra sulfur, a thing easily done by the disulfides, has based his theory on the disulfide being the active agent in the mechanism of these compounds as accelerators. On the other hand Bedford and Sebrell from the results of their work came to the conclusion that the metallic dithiocarbamates and their polysulfides were the active accelerating agents.

Whitby, G. S. and Walker, O. J. (1) have noted the differences in accelerating power of amine dithiocarbamates when used with and without zinc oxide. A more extensive investigation of the effect of using zinc oxide in varying amounts with a large number of amine dithiocarbamates, their metallic salts and disulfides has been made by Twiss, D. F., Brazier, S. A. & Thomas, F. (1). They found that in every case the presence of excess zinc oxide was essential to the best results.

It had previously been found, as stated above, that the zinc alkyl dithiocarbamates were more powerful accelerators than the corresponding amine salts or the disulfides. Twiss in his work found these salts to be of no practical value unless used in the presence of zinc oxide, and he at once raised the question as to whether such zinc salts were really the active agents which were responsible for the mechanism of the accelerating action. In fact he is somewhat doubtful of the entire theory as proposed by Bedford and his coworkers in their explanation of the action of accelerators. It has been shown that sulfur reacts with aldehyde ammonia in alcoholic solution with the formation of ammonia and hydrogen sulfide. This reaction was suggested by the hydrogen sulfide-polysulfide theory as the basis of the action of this compound as an accelerator. Twiss believes that although this reaction will take place in alcohol it is no assurance that the same reaction will take place in rubber. Similarly the evidence that zinc oxide will react with an amine alkyl dithiocarbamate dissolved in benzene to form the corresponding zinc dithiocarbamate

did not constitute definite proof, according to Twiss, that this compound was the active agent when amine dithiocarbamates or thiuram disulfides were used as accelerators. In other words, reactions which take place outside the rubber mix, may not always take place within such a mixture.

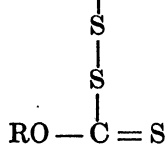
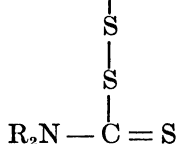
In view of the above facts Twiss concluded that the zinc salts were as unlikely to be the active catalysts as the original amine alkyldithiocarbamates or disulfides. He is inclined to the belief that some decomposition product, common to all three classes of compounds, and formed only in the presence of zinc oxide is the active compound.

The objections thus raised by Twiss have been further considered by Bedford, C. W. & Gray, H. (1). They have brought forward additional proof to show that the zinc salts of the alkyldithiocarbamates are the active agents in causing acceleration when amine dithiocarbamates or thiuramdisulfides are used as vulcanization catalysts. They point out that Twiss overlooked the action of the hydrogen sulfide, formed during vulcanization, on the metallic salts. It had been already shown, as mentioned above, that hydrogen sulfide would decompose the zinc salt, forming the free dithiocarbamic acid and zinc sulfide. In the presence of excess zinc oxide the dithiocarbamate immediately reforms the zinc salt and the accelerating action proceeds as before. The need of the use of zinc oxide in conjunction with the dithiocarbamates and thiuramdisulfides is to act as a sort of buffer against the action of hydrogen sulfide, and to insure that a sufficient concentration of the zinc salt, or active accelerator, is maintained throughout the curing process. Hydrogen sulfide is continually destroying the active accelerator and zinc oxide is continually reforming it. Zinc oxide may even be replaced by any other zinc compound which will react with the accelerator to form the zinc salt. Such compounds as zinc stearate, zinc resinate or zinc oxalate have been used with dithiocarbamate accelerators and without any zinc oxide, in which case cures equivalent to those obtained with zinc oxide result. Here again we have further evidence that the zinc salts are the active agents when accelerators of this type are used. In view of the above described results it would appear that the mechanism of the accelerating action of the above series of compounds may safely be ascribed to the formation of the zinc salts and their subsequent reaction with sulfur to form polysulfides.

Another series of compounds which have long been known to accelerate vulcanization and which resemble the dithiocarbamates in many of their reactions are the zinc alkylxanthates. These compounds were first used as accelerators about 1916 by Ostromuislen-skii, I. (13). They work best at comparatively low temperatures, and like the alkyl dithiocarbamates require the presence of zinc oxide for the attainment of their full power. In discussing these com-

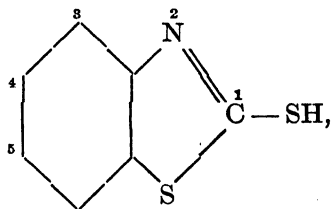
pounds Bruni has stated that with sulfur they react to form dioxanthogens, compounds having a structure analogous to the thiuram-disulfides.

Thiuramdisulfides,  $R_2N-C=S$ .    Dioxanthogens,  $RO-C=S$ .



These dioxanthogens would, according to Bruni's theory, be the active agents in the accelerating action of the xanthates. Little further work has been done on their reactions with the exception of that of Winkelman, H. A. & Gray, H. (1), who studied their decomposition products and concluded that the accelerating action was not due to any such product but probably to the action of the entire molecule itself. A large number of metallic alkylxanthates have recently been patented by Cadwell (*loc. cit.*), who uses them in the presence of aniline, whereupon their curing action at ordinary temperatures is greatly increased.

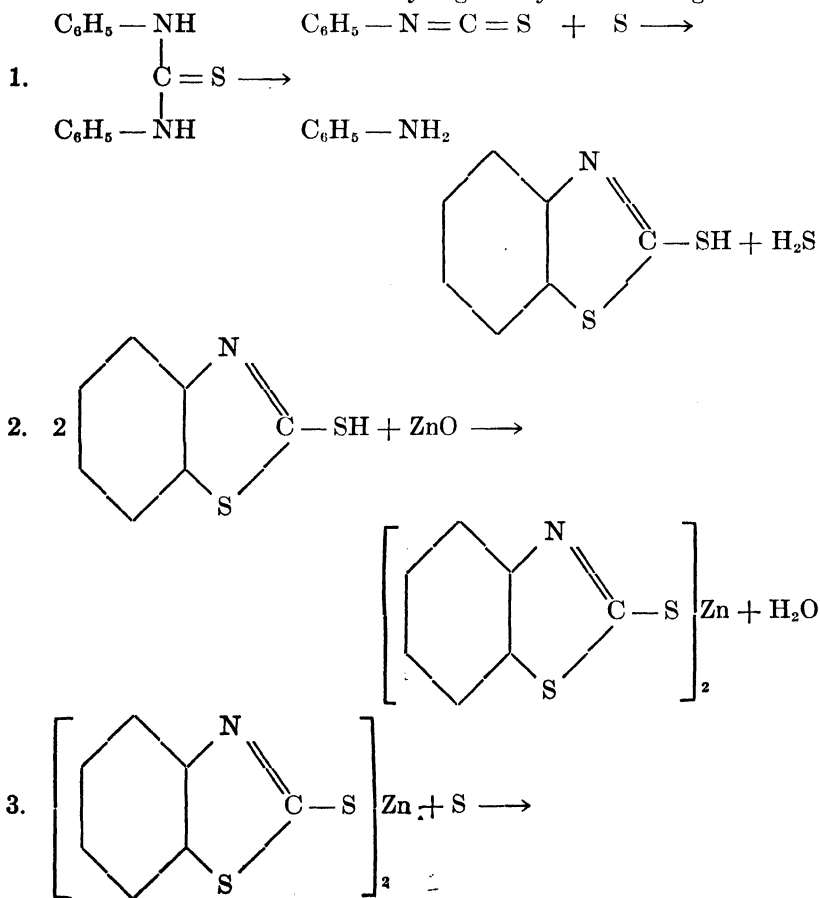
Another class of powerful accelerators which have recently been discovered are the mercaptothiazoles. The first member of the series was first shown to be an accelerator by the writer and the results published by Bedford and Sebrell only a few days before the announcement of a similar discovery by Bruni in Italy. It is indeed a strange coincidence that two laboratories so widely separated should independently come upon these compounds at about the same time. 1-Mercaptobenzothiazole,



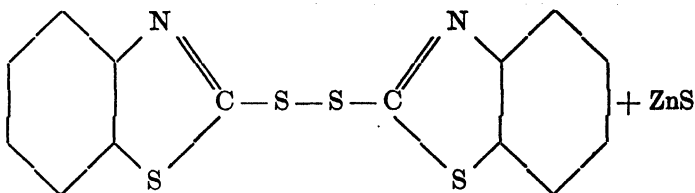
easily forms metallic salts with soluble zinc or lead compounds which are more powerful accelerators than the free thiazole. The disulfide also is easily obtained from the free mercaptan by oxidation, but is a less powerful accelerator than the free compound. It is necessary with all of these derivatives to use an excess of zinc oxide, as without it they show little accelerating power. In this respect they resemble exactly the dithiocarbamates already described. Bedford and Sebrell have therefore described the mechanism of the action of the mer-

captobenzothiazoles as being through the polysulfides of the metallic salts. The excess of metallic oxide which is necessary, insures the stability of the metallic salt and prevents its decomposition by hydrogen sulfide. The mechanism of their action as accelerators is thus entirely analogous to that of the dithiocarbamates.

Bruni compares the action of these compounds as accelerators to the dithiocarbamates as was done above but he is of the opinion that the disulfide is the active accelerator. The only preparation of 1-mercaptobenzothiazole recorded in the literature (Ber. 24, 1400), was by the action of sulfur on phenyl mustard oil. Bruni has assumed that through this reaction he is enabled to explain the accelerating action of thiocarbamilide as well. His theory is given by the following reactions:





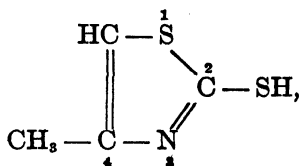


4. Disulfide + heat  $\longrightarrow$  Monosulfide + S (active)

According to this mechanism phenyl mustard oil should be more active than thiocarbanilide. This we know is not the case and for this reason we are inclined to doubt such an explanation. Further, the writer has found that the zinc salt of 1-mercaptobenzothiazole will air cure a cement in a few hours which the disulfide will not do even on standing several months. If the disulfide is treated with a small amount of hydrogen sulfide it will slowly air cure, although not as fast as a sample of tetramethylthiuramdisulfide under the same conditions. It would thus appear that the action of the mercaptobenzothiazoles and their derivatives are exactly like those of the aminedithiocarbamates, their metallic salts and disulfides.

Some further work has been done, by Sebrell, L. B. & Boord, C. E. (1), on 1-mercaptobenzothiazole by substituting various alkyl groups in the benzene ring and noting the resulting effect upon the activity of the compound as an accelerator. The results showed that the 3-methyl derivative was the most powerful and that the others ranked as follows: 3,5-dimethyl, 1-mercapto, 5-methyl, and 5-ethoxy. New methods of preparing the thiazoles were also given among which may be mentioned the preparation from the free base, carbon bisulfide and sulfur, and from the ammonium and zinc salts of the several dithiocarbamic acids. All the reactions were conducted under pressure in an autoclave. The original method by which 1-mercaptobenzothiazole was first discovered, i.e., by heating the disubstituted thiourea with sulfur under pressure, was also used in many cases. Romani, E. (2), has also described the three methyl mercaptobenzothiazoles but in his work he used only the thiourea method of preparation. It has been further shown that any substitution of the sulfur atoms in either the mercapto group or in the thiazole ring itself, will practically destroy the accelerating power of these compounds.

Another thiazole compound, 2-mercapto-4-methylthiazole,



has recently been discovered by Bruni, G., & Romani, E. (2). They found that the free thiazole, and its metallic salts are equally efficient in accelerating vulcanization as the mercaptobenzothiazoles. It is important to note that with this compound only the monosulfide and not the disulfide was obtained on oxidation. Bruni does not state whether this monosulfide is an accelerator or not. This compound should be just as powerful as the disulfide of mercaptobenzothiazole, if his theory for the mechanism of this type of accelerators is correct.

The last and most recently discovered carbosulphydryl accelerators are the dithio-acids, their disulfides and metallic salts. These compounds were first discovered by Cadwell, but Bruni, together with Romani (*loc. cit.*), have been able to develop methods of preparation which may be used for the production of these compounds on a somewhat larger scale. Perhaps the most important compounds of this group are dithiobenzoic and dithiopyromucic acids and their derivatives.

The method for the preparation of these dithio-acids consists in treating the corresponding aldehyde in alcohol with moderately concentrated ammonium sulfide solution. The alcohol is then removed by distillation, the residue poured into water and extracted with ether. The ether extract contains the free acid, which in most cases is very easily oxidized to the disulfide. Romani has shown that if one of the sulfur atoms in the  $\text{—C—SH}$  group is replaced with an



oxygen atom, the curing power is destroyed. This is analogous to the results already obtained with mercaptobenzothiazole. In general, the dithio-acids and particularly their zinc salts, will cause vulcanization at ordinary temperatures. They are therefore to be classed among our most powerful accelerators and more complete information concerning them will probably be available in the near future.

#### Nitroso Accelerators.

We cannot close our discussion of the mechanism of accelerators without some mention of those which contain the nitroso group. Among this group is at least one of the oldest and best known accelerators. Since they are not capable of the same reactions of either of the other two groups, we must consider them, as Bruni has done, as a separate group. It was thought at one time that hydrogen sulfide reduced the nitroso group to an amine group, whereupon the mechanism would then be as given above for any free amine. However, Stevens, H. P. (29), has pointed out that this explanation would be entirely insufficient, because while p-nitrosophenol acts as an accelerator, its reduction product, p-aminophenol has no such action. However, if p-nitrosophenol is reduced with hydrogen sulfide and treated with carbon bisulfide, an air cure of a

cement may be obtained, due to the formation of a dithiocarbamate.

The sulfur reaction of p-nitrosodimethylaniline has been found to liberate both hydrogen sulfide and sulfur dioxide which might possibly account for the curing action.

Bedford and Sebrell have attributed the curing action of nitroso accelerators to the oxidizing power of these compounds which facilitates the removal of hydrogen sulfide. They would thus resemble the secondary accelerators such as litharge. From the small amount of data at hand, as to the action of these compounds, it would seem that there is much yet to be done before we are able to satisfactorily explain the accelerating action of this type of compounds.

#### *Vulcanization at Low Temperatures by the Use of Organic Accelerators.*

The use of organic accelerators to promote vulcanization at room temperatures has been until very recently little more than a scientific curiosity. Such cures were used to prove several facts in relation to the various theories of acceleration and little practical use was made of them.

There is now a widespread feeling, which is becoming greater as time goes on, that there is a great field for the use of organic accelerators in curing rubber, not at 40, 60 or 70 pounds steam pressure, but at much lower pressures, such as 5, 10 or 20 pounds, and also even below 100° C. Rubber chemists are beginning to realize that rubber goods cured at a low temperature to the same physical state as similar materials cured at higher temperatures possess much better resistance to aging and superior wearing power.

It is generally believed that accelerators of the hydrogen sulfide-polysulfide class are not suitable for curing rubber at temperatures much below 140° C. The one exception to this statement is ethylidene aniline and its analogous compounds which work quite well as low as 120° C. Most all accelerators which work well at the lower temperatures are those of the carbosulphydryl group.

The first accelerators to be used in producing an air cure were piperidine, diisoamylamine and hexamethyleneamine. These compounds were used by Ostromuiskii, I. (14) to produce vulcanization at ordinary temperatures as already noted in this paper. He used them in conjunction with metallic oxides and obtained a cure at room temperatures in periods of time varying from two weeks to a month. The time of cure was greatly reduced by heating to 40° C. for forty minutes. He also extended these experiments on vulcanization to the amine dithiocarbamates which produced air cures containing as much as 3 per cent of combined sulfur after standing for three days. The work of Bruni, G. (3), on the vulcanization obtained by exposing an aniline-zinc oxide stock to carbon disulfide vapors has likewise been previously described.

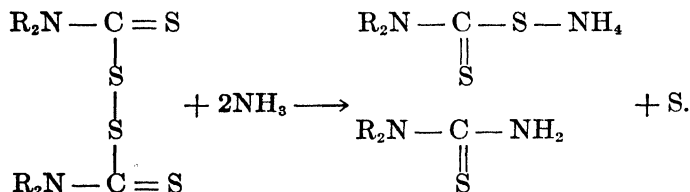
The use of accelerators for producing cures at low temperatures has not until recently been of general practical application, the reason being that any accelerator powerful enough to carry on the vulcanization at ordinary temperatures will cause a partial vulcanization during the preliminary treatment of the rubber. Two or three ways of overcoming this difficulty may be mentioned. Pestalozza, I. R. J. 65, 238 (1923), has described a process wherein the high powered accelerator is mixed into the rubber together with the desired metallic oxides. The articles to be cured are then formed and powdered sulfur dusted over the surface. On heating to 50-60° F. the sulfur dissolves in the rubber and vulcanization takes place easily and quickly. Dr. Bruni is authority for the statement that this method has been in use in Italy for several years and that good results have always been obtained with it. It has the advantage of never giving an "overcure."

Another method closely analogous to the one just described has been patented by Morton, H. A. & Harrison, M. M. (1). This method consists in mixing the rubber, sulfur and metallic oxide together, forming the article and dusting the powdered accelerator over the surface of the rubber. The accelerator upon diffusing into the rubber sets up the vulcanization action.

Cadwell in his patents (*loc. cit.*) finds that the several xanthates and dithiocarbamates also vulcanize at temperatures below 100° C. and that this action is increased by the addition of an aromatic amine.

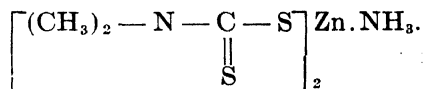
The use of tetramethylthiuramdisulfide as an accelerator for use in cures at 125° C. has been found to be satisfactory. It has not thus far been applied directly to the curing of rubber at temperatures of 80° C. or lower.

Bedford and Gray (*loc. cit.*) noted that Fromm, Ann. 348, 144 (1906), had made extensive experiments showing that disulfides which contained the group  $\begin{array}{c} \text{—C—S—S—C—} \\ || \qquad \qquad || \end{array}$  were acted upon by ammonia, aniline and other amines according to the following equations:



This equation afforded an explanation for the increased activity of such sulfides when treated with aniline, and gave suggestions for the activation of tetramethylthiuramdisulfide so that this accelerator might be made to cure at ordinary temperatures. Experiments showed that if a tetramethylthiuramdisulfide stock containing zinc oxide was treated with dry ammonia gas that an air cure was obtained in

about a week. The ammonium salt formed, as shown above, reacts with the zinc oxide to form the zinc dithiocarbamate which as we know will produce an air cure. It was further found that the zinc salt of dimethyldithiocarbamic acid would form an addition product with one molecule of  $\text{NH}_3$  corresponding to the formula



Stocks which contained zinc dithiocarbamates were found to air cure more quickly if exposed for some time to an atmosphere of ammonia gas.

The activation as above described renders practical the use of tetramethylthiuramdisulfide as an accelerator for producing vulcanization at temperatures below  $100^\circ \text{C}$ . Stocks containing as little as 0.5 per cent of this accelerator, after treatment with ammonia, will cure, as stated above, in a week at room temperature, while if the temperature is raised to  $80\text{--}90^\circ \text{C}$ . vulcanization can be secured in a few minutes.

In conclusion something should be said in regard to the determination of the "scorching" or set-curing action of accelerators. This is an important consideration from a factory standpoint in the use of various types of compounds.

Perhaps the best way of determining the relative scorching or set-curing power of an accelerator has been given by Bruni at the spring meeting of the American Chemical Society in New Haven, 1923. In comparing two accelerators by this method they are compounded into two different rubber stocks which are then milled to the same degree of plasticity. One at a time they are transferred to a closed chamber immersed in an oil bath kept at a constant temperature. Carbon dioxide is then admitted to the chamber under pressure which forces the stock through a small opening in the opposite end of the vessel. The set-curing action of any accelerated stock may easily be determined at any given temperature by weighing the amount extruded per unit of time. As the stock begins to cure or scorch a smaller amount is forced out during the given time interval. A comparison of the curves thus obtained with a series of accelerators affords not only a measure of their set-curing action but can be also used to determine their relative plasticity.

Cadwell has a somewhat similar method which may be described as follows. Test tubes are dipped in cements containing the various accelerators to be tested. After a uniform film has been built up the tubes are heated at constant temperature in an atmosphere of  $\text{CO}_2$ . The time of set cure was observed by examination of the different samples. It was stated that the use of  $\text{CO}_2$  was necessary to give the best results since it prevented oxidation of the accelerators.

## THEORIES OF VULCANIZATION

BY

DR. W. J. KELLY

The most important step in the manufacture of rubber articles is the vulcanization. This consists in heating together the sulfur and rubber for a definite length of time under definite temperature conditions or else the exposure of the article to sulfur monochloride either in solution or vapor, the latter usually at temperatures slightly above that of the atmosphere. Many attempts have been made to explain the action of these two vulcanizing agents but thus far no one theory explains all the known facts. Before discussing the existing theories in detail it is necessary to define what is meant by vulcanization. During the treatment with sulfur or sulfur chloride the rubber goes through a progressive change which is characterized by its physical properties. It becomes less and less soluble in the solvents for crude rubber, its plasticity decreases and its strength, its resistance to stretching, abrasion and the action of chemical agents increase. In short it assumes all the well known and characteristic physical properties of vulcanized rubber. These changes may be brought about by other agents such as chlorine, bromine, iodine, selenium, tellurium, the hydrogen-halides, oxygen, ozone, etc. However, as the products obtained from the action of these substances are of no commercial importance at present, their discussion will be limited, except in so far as their behavior might throw some light on the action of sulfur or sulfur monochloride. Thus we may for present purposes define vulcanization as the change in physical properties due to the action of sulfur or sulfur monochloride on rubber. It will thus be seen that this definition considers only the result and is independent of any theory concerning the mechanism of the process by which that result is obtained. What we shall attempt to do in this chapter is to explain the mechanism of this change in the light of the known facts and the existing theories. The word "cure" is often used synonymously with vulcanization but more properly it designates that particular degree of vulcanization which yields a product of commercial value. The terms "under cure," "over cure" and "proper or optimum cure" have meanings which are obvious from the expressions themselves.

*Theories of Vulcanization.*

The theories which have been advanced in explanation of the mechanism of vulcanization may be classed under three main headings as follows:

1. Physical theory.
2. Physical-chemical or adsorption theory.
3. Chemical theory.

The order in which they are given has no bearing on their importance or validity but it seems best to discuss them in that order. The second and third have received much more attention than the first probably because they are more plausible and cover more of the known facts than the first one. No one of them alone covers all that is known about the mechanism of this process. For this reason the attempt will be made here to discuss each one in detail, point out its strong and weak points and then by correlating what is known, suggest a theory which is more comprehensive and which, it is hoped, will indicate new lines of attack on this important problem. The above refers to both the sulfur or hot process and the sulfur monochloride or cold process.

Naturally it will be necessary to discuss somewhat the action of accelerators and the new gas cure with hydrogen sulfide and sulfur dioxide invented by Peachy, but these will find their proper places as the evolution of the theories progresses.

*The Physical Theory of Vulcanization.*

The Physical theory is a very old one and was doubtless conceived because of the fact that it was impossible to discover any mathematical relationship between the amount of unextractable sulfur and the physical properties of the vulcanized product. In other words, it is not possible to say that a definite amount of combined sulfur is absolutely necessary to obtain the best physical results, or that any given amount predetermines certain physical tests. The same amount of such sulfur in different batches of the same rubber may give widely different physical properties. This fact led Höhn, J. B. (1), to state that, as a result of his experiments, "Vulcanization is not a chemical reaction but the molten sulfur is taken up by the cells of the rubber and forms an alloy, if it may be so named, the physical properties of which are different from those of the original material."

Weber, C. O. (61), p. 93, also states that many of the older writers even went so far as to deny the possibility of a chemical reaction taking place at all, and these men again based their statements on the absence of the definite relation between unextractable

sulfur and physical properties. With the introduction of accelerators, especially the so-called ultra-accelerators the variation in this relationship has become even greater and hence, although not explained by the physical theory, the facts must find their proper places in any comprehensive theory. This point will be discussed later under the other theories. The physical theory did not remain long in favor, and as it explains practically nothing it is not worth while to discuss it further.

### *The Adsorption or Physical-Chemical Theory of Vulcanization.*

The adsorption theory as proposed by Ostwald, Wo. (1), is an attempt to explain the known facts concerning vulcanization on the assumption that the rubber adsorbs the sulfur but that there is no chemical reaction between the two resulting in the formation of a definite chemical compound as first proposed by Weber, C. O. (61), p. 92. Ostwald uses the data published by Minder, J. (4), Weber, C. O. (39a) & (63), Höhn, J. B. (1), Markwald, E. & Frank, F. (4), Ditmar, R. (23), and others. Ditmar accepted the cyclooctadien formula of Harries, C. (9), and with this as a basis worked out the whole series of sulfur and sulfur chloride addition products. Erdmann assumed that there was an eight membered ring in the sulfur molecule  $S_8$  and that, on account of its similarity to the eight membered ring of the Harries formula, the two substances would react very easily forming thiozonides. Both of these views had to be abandoned in the light of the later work of Harries, C. (25), who now proposes a 32 or 40 membered ring as the lowest to be found in rubber.

Referring directly to Ostwald's publication we find that he takes up different facts in a rather systematic way and attempts to show that they can be better explained on an adsorption basis than on a strictly chemical one. The first of these facts is that irrespective of the amount of sulfur used or the duration of the heating there is always some so-called free sulfur left which may be extracted by suitable solvents. Even with very small amounts of sulfur which it might be expected would be entirely used up by the rubber, some sulfur can still be extracted with acetone. This points, according to Ostwald, to the fact that the sulfur does not form a stable compound with rubber but is merely adsorbed by it and that continued extraction will remove sulfur until there is none left. In other words, in the presence of the solvent there is an equilibrium between the sulfur adsorbed by the rubber and its concentration in the solvent. This point of Ostwald's is based on faulty data. In the first place it has never been shown by anyone that exhaustive extraction will continue to yield *elemental* sulfur. The sulfur extracted has always been determined by oxidizing the residue and hence the sulfur might



have been present in some organic body only slightly soluble in the acetone. It is not at all an impossibility that the vulcanized rubber itself might be sufficiently decomposed by long extraction and attendant oxidation to render it sufficiently soluble in acetone to yield some small amount of sulfur by this method. Spence, D. (19), has shown that all of the soluble sulfur may be extracted, and Spence, D. & Ward, C. A. (1), have shown that all of the sulfur may be made to combine with the rubber. Lately Stevens, H. P., R. Age (London) 4, 194 (1923), has shown that there is no difference between the amounts of sulfur remaining insoluble in acetone at the end of one week's extraction and at the end of nine weeks' extraction. The figures in Table I show the percentage of sulfur left after the extractions.

Table I.

Time	% S
1 week .....	1.54
2 weeks.....	1.54
4    "    .....	1.47
9    "    .....	1.55

The writer, Kelly, W. J. (1), has also shown that the resins and proteins react with sulfur to form products soluble in acetone and hence it might be expected that there would always be some sulfur present in the acetone extract, but not necessarily *elemental* sulfur. It has also been shown by the author (*loc. cit.*) that alcoholic KOH will remove more sulfur after completion of the extraction with acetone but that repeated treatments of the same sample yielded no trace of sulfur after the second extraction. If the sulfur is adsorbed and an equilibrium exists between the sulfur in the acetone and that in the rubber, a similar equilibrium should exist between the rubber and the alcoholic KOH, except in this case it would be displaced in favor of a larger amount of sulfur in the alcoholic KOH than in the acetone due to the reduction of the elemental sulfur by reaction with KOH. No such action takes place and as mentioned above repeated extractions fail to remove even the slightest trace of sulfur. It would seem that this fact alone would dispose definitely of the adsorption theory but there are more points to be cleared up before this theory is finally discarded. Höhn, J. B. (1), described another experiment which Ostwald uses as an argument in favor of adsorption. Höhn claims that on dissolving rubber in benzine and evaporating the solution he always obtained some crystals of sulfur no matter how often the process was repeated. This fact could be explained equally as well by assuming a decomposition and dissociation or by imperfect extraction, as it could by the reversal of an adsorption. In the light of what has been said above it would seem that Höhn's technique

was at fault. Weber, C. O. (8), Marckwald, E. & Frank, F. (4), Axelrod, S. (1) and Anon. (230), all disputed the fact as described by Höhn.

The next point in Ostwald's exposition of his theory is that sulfur adds on directly to the rubber and does not substitute any hydrogen with the consequent evolution of hydrogen sulfide. This fact alone is no more satisfactorily explained by adsorption than it is by chemical reaction. A similar case of sulfur adding on to the double bond of a carbon compound is to be found in the sulfurized or vulcanized oils which are called rubber substitutes. On saponifying these oils the sulfur goes quantitatively with the acid which it most certainly would not do were the sulfur only adsorbed by the oil. In the case of sulfur chloride Ostwald also claims that the facts are better explained by assuming that the sulfur is adsorbed and the chlorine set free. In other words there is a selective adsorption strong enough to break up the  $S_2Cl_2$  molecule. This is hardly possible but as a parallel case Ostwald cites the selective adsorption of potassium ion from solutions of its chloride, acetate and sulfate by manganous hydroxide. There is no parallelism between these cases as with the potassium salts we are dealing with a dissociated substance whereas sulfur chloride does not dissociate into S and Cl in rubber solvents. Assuming for the moment that chlorine were set free, it would most certainly add on to the double bonds of the rubber as chlorine is very active in exactly this way. Höhn noticed that the chlorine content of a sulfur chloride solution increased after being used several times for vulcanization. This is easily explained by the presence of moisture in the rubber which reacted with the  $S_2Cl_2$  to generate  $SO_2$ ,  $H_2S$  and  $HCl$  and likewise to precipitate some sulfur. The action of the rubber resins on the  $S_2Cl_2$  would also generate  $HCl$  as it is fairly certain that these resins contain hydroxyl groups.

The principal objection that Ostwald has to the chemical theory is the assumed formation of a series of compounds containing different amounts of sulfur the highest of which,  $C_{10}H_{16}S_2$ , according to Weber, C. O. (61), p. 92, contains 32 per cent of sulfur. The lowest member according to Weber's theory would be  $(C_{10}H_{16})_{10}S$  containing 2.3 per cent of acetone insoluble sulfur.

Weber himself does not state that an absolutely definite compound of this formula is the lowest of the series and says that it is impossible "at present" to isolate the lowest member. To quote from Weber: "In view of the circumstance, however, that the important change produced by vulcanization in the production of soft rubber goods becomes first clearly apparent when the vulcanized india rubber contains from 2 to 2.5 per cent of sulfur, we may assume that this represents the lowest limit of the possible polyprene sulfides."

Ostwald claims that, on account of the fact that there are no definite breaks in the sulfur-time curve and that no one has yet

succeeded in isolating any of the compounds, the whole process can be accounted for more satisfactorily on the adsorption basis than by a chemical reaction. The fact that no one has succeeded in regenerating sulfur-free rubber from the vulcanized rubber is no argument against adsorption as many cases of irreversible adsorption are known. As to the breaks in the sulfur time curves obtained by Weber, it has been shown many times that these were due to faulty experimental methods. The relation between time and the amount of unextractable sulfur is in nearly all cases a straight line up to the point where the sulfur is practically exhausted. If the process is one of adsorption it should follow the adsorption isotherm and the relation between the free sulfur and the acetone insoluble sulfur should be expressed by the Freundlich equation

$$x = k.c^{\frac{1}{n}}$$

where (x) is the amount adsorbed and (c) the concentration of the free sulfur, (k) and (n) being constants. A glance at this equation will show that there is no time factor in it. In other words it represents an equilibrium condition and could be applicable only to a given cure. However, at no point on the vulcanization curve does equilibrium between free and acetone insoluble sulfur exist. The process of sulfur absorption is continuous and goes without stopping until all of the sulfur present has been taken up by the rubber as shown by Spence, D. (19) and Spence, D. & Ward, C. A. (1). The largest amount possible is 32 per cent of the total or 47 parts per 100 of rubber. Some cases have been noted in the literature where more sulfur than this has been found to be unextractable. Weber, C. O. (61), p. 91, states that he once obtained a product with 38.18 per cent of sulfur but this product was porous and brittle indicating that a gas, hydrogen sulfide, had been evolved. It is naturally not impossible for the sulfur to substitute some hydrogen towards the end or after all of the double bonds have been saturated and in this way yield a product with more than 32 per cent of sulfur. Spence, D. & Young, J. (1), working with extracted rubber were unable to obtain products with more than 32 per cent of sulfur and hence the cases where more than this were found may also have been due to the insoluble sulfur-resin or sulfur-protein compounds formed. Thus it seems to be generally accepted that a product containing more than 32 per cent of sulfur cannot be obtained if there is no decomposition of the rubber attended by an evolution of  $H_2S$  and if the formation of insoluble compounds from the resins and proteins is taken into account.

Reverting again to the adsorption formula, this states that at equilibrium the amount adsorbed increases as the concentration of the adsorbed substance in the solution is increased. In any process

of vulcanization the amount of insoluble sulfur increases as the concentration of the free sulfur decreases, and at no time has any satisfactory mathematical relationship between the insoluble and the soluble sulfur been found which is applicable to the entire range of the particular vulcanization. Spence, D. & Young, J. (1), found the following expression to hold,

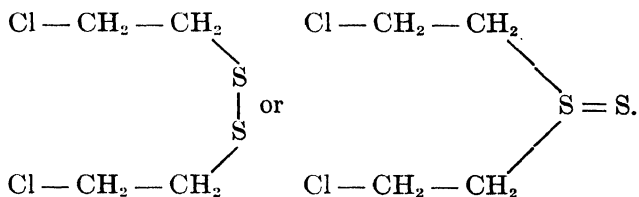
$$k = \frac{x}{t}$$

where (x) is the amount of insoluble sulfur, (t) the time and (k) a constant. In this equation  $x/t$  is the slope of the curve and the fact that it is a constant is obvious from a glance at any combined sulfur/time plot, the line being straight in all cases. The value of  $x/t$  will vary according to the conditions of the experiment but will in all cases be a constant.

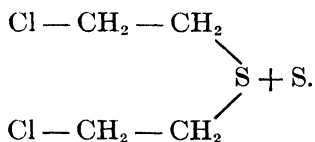
Bysow, B. V. (4), has also attempted to show that for definite time and temperature of vulcanization the ratio of total to free sulfur is a constant. The limits within which he calls the constant "constant" are rather wide. In one case it varies from 1.14 to 1.99 and in another from 2.17 to 3.65 and depends as well on the total amount of sulfur used. Hence it is natural to doubt the validity of the statement that the ratio of the total to the free sulfur is a constant.

Another point which Ostwald uses in support of the adsorption theory is the temperature coefficient of vulcanization. Calculating from Weber's results, which are admittedly wrong, Ostwald obtains the value of 1.8 for the temperature coefficient. According to van't Hoff's law this coefficient for a chemical reaction varies between 2 and 3.5. Ostwald claims that the value of 1.8 for vulcanization agrees much better with the value of the temperature coefficient for the adsorption of congo red by filter paper which is 1.36 than it does with that for a chemical reaction which may be as low as 2. The deduction seems to be slightly overdrawn. However Twiss, D. F. (4), has recently shown that the temperature coefficient is about 2.6 whether calculated from physical properties or from the amount of insoluble sulfur. Spence, D. & Young, J. (2), find the coefficient to be about 2.8. Both of these figures fall at about the average called for by van't Hoff's law and hence Ostwald's deduction from Weber's results must be discarded, and the view adopted that the temperature coefficient favors a chemical reaction rather than an adsorption. It is possible that temperature coefficients of adsorption processes may come within the range of those of chemical reactions especially in view of the fact that for adsorption these coefficients have rather a wide range extending from negative to positive. The magnitude of this coefficient, however, can only be used as an indication of chemical reaction at present.

With  $S_2Cl_2$ , Hinrichsen, F. W. & Meisenburg, K. (1), found that the "end product" which they obtained varied widely in sulfur content, the figures running from 15.58 to 28.37 per cent. This, Ostwald argues, is another point in favor of the adsorption theory as it shows that the composition of the end product is indefinite. Bysow, B. V. (1), working with dilute solutions of  $S_2Cl_2$  (benzol) and immersing a strip of rubber in the solution was unable to show an end point to the reaction unless very small amounts of  $S_2Cl_2$  (0.1 g. per 100 cc.) were used. Even in this case the figures indicate that equilibrium had not been reached at three hours although Bysow claims that it is attained at the end of one hour. The slowness of increase in the amount of sulfur taken up by the rubber indicates that all of that absorbed was at the surface and that the diffusion to the interior is a very slow process even with strips only 0.5 mm. thick. On the other hand, Hinrichsen, F. W. & Kindscher, E. (1), working with larger relative amounts of  $S_2Cl_2$  showed that the sulfur content of the product obtained was independent of the amount of  $S_2Cl_2$  used provided this were large enough to completely saturate the rubber. In addition they also used a solution of rubber, thus obviating the diffusion trouble. According to their results, rubber absorbs one half its weight of  $S_2Cl_2$  and thus considering rubber as  $(C_{10}H_{16})_n$  with a molecular weight of  $(136)_n$ , it is concluded that two molecules of rubber react with one of  $S_2Cl_2$  (m. w. 135) to give a product  $[(C_{10}H_{16})_2 \cdot S_2Cl_2]_n$ . This is in accord with Guthrie, *Ann.* 113, 270, who obtained products of an analogous structure from ethylene and amylene by the action of  $S_2Cl_2$ . These substances are given the formula



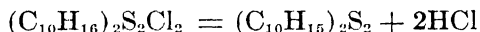
The recent results obtained on "mustard gas" indicate that the second formula is correct and that the extra sulfur atom splits off giving



There is no reason for assuming that the ultimate size of the rubber molecule is  $C_{10}H_{16}$  and hence this deduction of Hinrichsen & Kindscher

cannot be accepted. Assuming the 32 C-atom ring as the simplest in rubber, we should then have two molecules of  $S_2Cl_2$  combining with four of the eight double bonds of the ring. This would leave four of the double bonds free. If we assume that the one sulfur atom splits off as is the case with "mustard gas" this sulfur would be in its most active form and it is reasonable to suppose that it might then saturate two more of the double bonds of the rubber. It would be interesting to brominate this product to determine its unsaturation. If four molecules of bromine were taken up for every  $C_{40}H_{64}$  group we should be inclined to adopt the symmetrical form of  $S_2Cl_2$ , whereas if only two molecules were absorbed it would be definite proof that the sulfur splits off and then saturates another of the double bonds.

If, as Ostwald maintains, the sulfur chloride is adsorbed by the rubber, it is questionable if the chlorine could be removed by means of alcoholic KOH, leaving the sulfur untouched. If  $S_2Cl_2$  were adsorbed, one might expect that it would react with the water or alcohol giving free sulfur,  $H_2S$  and  $SO_2$ . Such is not the case and according to Hinrichsen, F. W. & Kindscher, E. (1), the product thus obtained having a definite sulfur content. By analysis they found 20.57 per cent S, whereas the theory, figuring on



a value of 19.1 per cent would be required.

Hinrichsen and Kindscher give the formula above as  $C_{20}H_{32}S_2$  but this is incorrect as the alcoholic KOH removes hydrogen chloride and hence the formula should be  $C_{20}H_{30}S_2$ .

With regard to the relation between physical properties and amount of insoluble sulfur Ostwald quotes some figures from Axelrod, S. (1), on the effect of heat. Axelrod milled two samples of the same rubber, one of which, B, had been heated  $\frac{1}{2}$  hour at  $120^\circ$  before mixing, then vulcanized pieces at  $130^\circ$  and  $135^\circ$  C. The samples were then analyzed for insoluble sulfur and the following figures obtained.

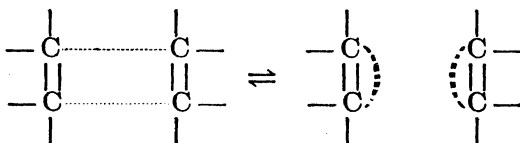
	130°		135°	
Time	A	B	A	B
30.....	0.99	1.24	1.71	2.15
60.....	1.99	3.08	3.23	3.50
90.....	2.65	3.29	3.59	5.35
120.....	3.10	3.50	4.76	5.97

Ostwald remarks that he cannot understand why, according to a chemical theory, the rubber which has been milled and thus depolymerized, should be able to "bind more sulfur than the whole molecule." The statement has never been made that depolymerized rubber will combine with *more* sulfur than the original or less depoly-

merized rubber. The difference in behavior of the two mixings of Axelrod is not in the *amount* of sulfur taken up but in the *rate* at which it is absorbed. It is a fairly general phenomenon that if a substance exists in two states of polymerization, the lower state is more active chemically than the higher, and hence if rubber is depolymerized by heat and milling it is natural to expect that the rate at which it absorbs sulfur will be greater in the depolymerized state.

Spence, D. & Ward, C. A. (1), repeated the work of Axelrod but found that the previous heating had no effect on the rate at which sulfur was absorbed by the rubber. Rossem, A. van (6), also showed that mastication had no effect on the rate of sulfur addition on samples whose viscosity in 5 per cent benzol solution was reduced from 177 to 63 by milling. This point, however, requires further study in the light of the foregoing paragraph.

"Depolymerization" and "polymerization" are two terms which are widely used in discussions on rubber. Their application to the behavior of rubber is not strictly logical and it might be well at this point to show why another term would be better. Originally polymerization referred to the union of two or more molecules of a given substance to form a new compound of identical composition but different structure and having a molecular weight which was a simple multiple of that of the original substance. This union is always accompanied by a rearrangement in the linkages as shown by the polymerization of acetylene to benzol, formaldehyde to paraldehyde, etc. In the case of rubber we cannot definitely say that there is no rearrangement of the linkages as the rubber is depolymerized. However, the fact that, irrespective of the physical state of the rubber, whether milled for long times or dissolved in hot or cold solvents, rubber always absorbs the same amount of bromine,  $S_2Cl_2$ ,  $HCl$ , etc., would indicate that there is no change in the double bonds and it is difficult to see how a rearrangement of the single C-C linkages could take place. If we assume that partial valence plays a role in this phenomenon it might be possible to explain the behavior of the rubber on milling and heating according to the scheme



where the dotted lines represent the partial valencies.

However, as rubber must be considered as a polyphase system it is much more logical to explain its behavior as an agglomeration or aggregation. In this way the action of heat or milling would be merely an increase in the degree of dispersion of one or more of the

phases in the remainder of the rubber. Considering rubber as a poly-phase system each phase of which has the same empirical composition, viz.,  $(C_6H_8)_n$ , it is necessary to assume that in any given piece of rubber there are particles of varying sizes present and that these particles are not mutually soluble in all proportions. The word soluble here indicating molecular dispersion. Thus heat and chemical action merely change the relationships between the different phases which are characterized by a greater plasticity or softness and which can best be designated by "state or degree of aggregation or agglomeration."

If the dispersity of any substance is increased it is natural to expect that its activity, chemically speaking, would also be increased owing to the fact that a larger surface is exposed. This is naturally true of adsorption as well, but in either case it will explain why, as Axelrod found, a piece of rubber which has been worked excessively will absorb sulfur more rapidly than one which has not, and this change in the rate of absorption is not dependent alone on either a chemical or an adsorption process but is common to both.

Thus far the discussion of the adsorption theory has been limited to the mutual behavior of rubber and sulfur or sulfur monochloride. From the facts presented it is not easy to see how the process of vulcanization can be explained on this basis. To recapitulate, if the rubber adsorbs the sulfur, then at least part of the insoluble sulfur should be extractable by some solvent or chemical agent. This has never been definitely shown and in fact the most careful work has finally proven that the combined or insoluble sulfur cannot be removed without destroying the rubber molecule. Inversely there is no reason why an adsorbed layer of sulfur on the surface of the rubber particles should prevent the rubber itself from being dissolved in solvents which are also solvents for sulfur. It is well known that vulcanized rubber will not dissolve in the ordinary solvents for unvulcanized rubber unless the temperature is raised considerably. In this case the residue left on evaporation has none of the physical properties of the original. It has become soft and sticky and is practically without strength. Its sulfur content on the other hand remains the same and it is still impossible to extract further sulfur with acetone or other solvent in which the rubber is insoluble. This points directly to a further change in the state of aggregation of the rubber and this is probably a purely physical change which takes place independently of the sulfur.

Taking all the evidence into consideration, it may be definitely stated that the process of vulcanization is a pure chemical reaction and has none of the characteristics of an adsorption in so far as the relationships between sulfur or sulfur monochloride and rubber are concerned.

Ostwald neglects the fact, that after the action of  $N_2O_3$ , Cl, Br, etc., sulfur remains combined with the rubber. Caspari, W. A. (2)



and Hinrichsen, F. W. (5), both state that when derivatives of vulcanized rubber are made with Br,  $N_2O_3$ , etc., the sulfur remains quantitatively with the rubber. If the sulfur were only adsorbed by the rubber this would most certainly not take place.

There is another phase of the adsorption theory which may have a little more solid ground to stand on than the one just described. This theory has been put forward by Skellon, H. (1), Ostromuiskenskii, I. (15), Bernstein, G. (3), and others in an attempt to explain vulcanization. These authors consider that vulcanization is a chemical action which converts part of the rubber to a sulfur or sulfur chloride derivative, following which this derivative either swells in the remaining rubber or the remaining rubber swells in it. The main objection to this theory is that it is impossible by means of solvents to separate the two phases and if vulcanization is such a process it should be possible to separate the final product into two or more parts by means of solvents. Even in vulcanized rubber which has been dissolved by treating it with solvents at elevated temperatures no one has ever been able to show the presence of two or more bodies. From this Ostromuiskenskii reasons that any colloid which will be adsorbed by or swell in the rubber will cause vulcanization, and in support of this has shown that when oxidized rubber or rubber treated with hydrogen chloride to form the so-called dihydrochloride is mixed with fresh rubber and heated, the whole mass assumes the physical properties of vulcanized rubber. Harries, C. (28), has shown that at about 135° C. part of the HCl splits off from the dihydrochloride and it is possible in the experiment described by Ostromuiskenskii that this happened, the free HCl then adding on to some of the fresh rubber to form the so-called monohydrochloride which is stable at this temperature. The same explanation of the action of oxidized rubber may be sufficient. In the case of sulfur vulcanization this does not hold at all as otherwise it would be possible to vulcanize fresh rubber by merely mixing in some reclaimed rubber and heating it. This has never yet been done, although according to the adsorption theories it should be possible.

Still a third phase of the physical-chemical theory is that in which vulcanization is considered as a process taking place in two steps. The first of these is an adsorption of the sulfur by the rubber, and the second is a chemical reaction between the rubber and the adsorbed sulfur. This view is held by Ahrens, F. (6), Hinrichsen, F. W. (4), (5), Stern, E. (1) and others, but in this case the theory put forward is merely a combination of the chemical and the adsorption theories and does not explain anything in addition to the other theories. It has, however, been shown by Venable, C. S., & Green, C. D. (1) and also by the author,\* that sulfur is actually dissolved in the

\* Kelly, W. J. Paper read before the Rubber Division of the American Chemical Society at New Haven, Conn., in April, 1923. Not yet published.

rubber and hence in any chemical reaction between the two the first step must of necessity be the solution of the sulfur.

### *The Chemical Theory of Vulcanization.*

The chemical theory of vulcanization was first proposed by Weber, C. O. (61), p. 89, as a result of his experiments on the action of sulfur on rubber. According to Weber's theory the sulfur and the rubber combine to form a series of compounds which he called the polyprene sulfides. The only one of these to which Weber assigns a definite composition is the highest member of the series containing 32 per cent of sulfur and having the empirical formula  $C_{10}H_{16}S_2$ . Assuming the structure for rubber to be a ring, then for every  $C_{10}H_{16}$  there would be two double bonds. During the process of vulcanization there is extremely little or no hydrogensulfide evolved and thus Weber reasons that the sulfur adds directly on to the rubber and does not substitute any of the hydrogen. Weber also indicates that the lowest member of the series may have the composition  $(C_{10}H_{16})_{10}S$  but bases his conclusion on the fact that the important change in the physical properties is first clearly apparent when 2 to 2.5 per cent S has combined with the rubber. Weber puts this formula forward only as a suggestion and admits it has no justification chemically as no body of that composition has ever been isolated from vulcanized rubber.

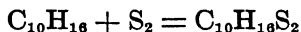
Ostwald, Wo. (1), objects to both these formulas but more particularly the highest member  $C_{10}H_{16}S_2$ , claiming that several investigators have had samples containing more than 32 per cent of sulfur. Spence, D. & Young, J. (2), Hinrichsen, F. W. & Kindscher, E. (4) and others, working with large amounts of sulfur, were never able to obtain a product with anything but 32 per cent of combined sulfur provided the vulcanization was carried on for a sufficient length of time. These results confirm those of Weber and hence it may be definitely stated that the end product of vulcanization has the formula  $(C_{10}H_{16}S_2)_n$ . Owing to the fact that his product is insoluble in all solvents it is impossible to determine its molecular weight and thus the value of  $n$ . If the rubber is completely disaggregated during the process of vulcanization the end product will probably be  $C_{40}H_{64}S_8$  or  $C_{50}H_{80}S_{10}$  according to the latest work of Harries, C. (25), who now considers the simplest rubber molecule as a ring containing 32 or 40 carbon atoms.

Van Iterson, G. (1), on the other hand, although he believes that sulfur and rubber combine chemically, does not agree that the end of the reaction has been reached when 32 per cent of sulfur is present in the final product. This is not so stated by any one. The fact is that no more than 47 parts of sulfur per 100 of rubber (32 per cent on the vulcanized mix), can combine without the evolution of hydrogen sulfide. Naturally more sulfur can combine as Weber found, but in

this case the reaction had gone beyond the addition stage and some of the hydrogen was substituted with a consequent evolution of  $\text{H}_2\text{S}$ . This, however, only takes place at higher temperatures and is usually accompanied by an evolution of heat as shown by Bysow, B. V. (3).

In spite of the fact that no one of the members of the series poly-prene sulfides suggested by Weber has been isolated, the theory of chemical combination explains more of the known facts than the adsorption theory. The fact that no one has yet succeeded in removing the combined sulfur from the rubber and at the same time leave the rubber molecule intact is one of the best arguments in favor of the chemical theory. Several attempts have been made to remove the combined sulfur but none has met with success. Hinrichsen, F. W. & Kindscher, E. (5), claim that they were able to reduce the sulfur in vulcanized rubber considerably by heating it in benzol with alcoholic KOH and copper or zinc in an autoclave. In the case of rubber vulcanized with  $\text{S}_2\text{Cl}_2$  and the chlorine removed with alcoholic KOH, they claim to have obtained a sulfur free product. For this case no figures are given but several analyses are presented in substantiation of the claim for the sulfur vulcanization. Alexander, P. (11), claims that the figures given by Hinrichsen & Kindscher do not prove that there was a diminution in the amount of combined sulfur and that in order to definitely settle the question similar experiments should be carried out on products of different degrees of vulcanization up to the highest, i.e.—with 32 per cent of combined sulfur.

Bary, P. & Weydert, L. (1), claim that the sulfur of vulcanization can be removed by heating the vulcanized sample to  $140^\circ$  in xylol and evaporating the solvent. They claim that in all cases they were able to show some extractable sulfur in the residue from such operation but fail to state whether or not it was elementary sulfur. They thus consider that vulcanization may be expressed by the equation



and that the removal of the free sulfur permits the reversal of the reaction. They also believe that there must necessarily be some equilibrium between the free sulfur, the rubber and the compound  $\text{C}_{10}\text{H}_{16}\text{S}_2$ , but state that the ordinary laws of mass action do not apply in this case.

Repony, D. (1), attempted to remove the sulfur from rubber by several methods but was forced to conclude that this could not be done. He tried nascent hydrogen from aluminum and caustic, zinc and caustic, zinc and acid and although vigorous actions were obtained he was unable to show any reduction in the amount of combined sulfur.  $\text{NaOH}$ ,  $\text{NaOH} + \text{Pb}$ ,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  or  $\text{Fe}$  heated in a rubber solution for 5-12 hours at  $140\text{--}170^\circ \text{C}$ . failed to reduce the sulfur content. Metallic sodium when mixed with the rubber reacted so violently that the whole mass was ignited.

If such powerful reagents as these fail to remove any of the combined sulfur, it seems impossible to explain vulcanization on the basis of adsorption of the sulfur by rubber. Again, how can the results of Bary & Weydert (*loc. cit.*) be explained except by assuming an oxidation or complete decomposition of part of the rubber thus rendering it soluble in acetone along with its combined sulfur?

It has been shown by several authors that when derivatives of rubber are made with  $\text{Br}_2$ ,  $\text{HCl}$ ,  $\text{O}_3$ , etc., the combined sulfur remains quantitatively with the rubber. If vulcanization were merely adsorption this would be rather hard to explain, especially if vulcanization with  $\text{S}_2\text{Cl}_2$  or  $\text{S}_2\text{Br}_2$  is also assumed to be purely adsorption.

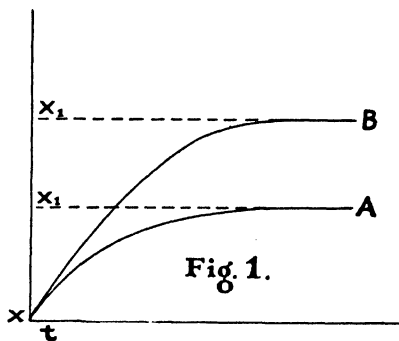
These facts all prove that the mutual action of sulfur and rubber can be best explained on a purely chemical basis. Furthermore, it has been shown by Venable, C. S. & Green, C. D. (1), and also by the writer (*loc. cit.*), that sulfur is molecularly dispersed in the rubber hydrocarbon or in other words it dissolves in the rubber and the resulting solution obeys Henry's law perfectly. The work of Endres, H. A., I.R.W. 68, 635 (1923), has also shown that the mixtures of rubber and sulfur exhibit other properties of true solutions such as crystallization, supersaturation and diffusion and also that in rubber all forms of free sulfur tend to go over to the rhombic form at ordinary temperatures.

The question now arises, can soluble sulfur suddenly change to the unstable form, become insoluble and then be adsorbed by the substance in which it was originally soluble? This is what would be required by the adsorption theory. Owing to the complexity of rubber and the accompanying substances it is possible that some reaction between the sulfur and the resins or proteins would generate the insoluble form of sulfur. However, Twiss, D. F. (4), has shown that both forms of sulfur have approximately the same action in vulcanization and also that after vulcanization all of the free sulfur from the sample cured with insoluble sulfur had become soluble in acetone, thus showing that the reverse of the above outlined process actually does take place in rubber.

As mentioned above some authors consider that the process of vulcanization takes place in two steps, the first of which is either solution or adsorption of the sulfur by the rubber and the second a chemical reaction between the two. It has already been stated that the sulfur first dissolves in the rubber in a molecular state and thus, as far as the rubber and the sulfur are concerned, the reaction takes place in a homogeneous system. This fact eliminates the objection of some authors, especially Stern, E. (1), that the laws of reaction rates cannot be applied to the vulcanization of rubber, on account of the fact that these laws apply only to homogeneous dilute solutions and not to colloidal systems. It follows that if the sulfur is molecularly dissolved in the rubber the laws of reaction rates should apply

and by this means a great deal of light might be thrown on the mechanism of vulcanization. The use of a common solvent for rubber and sulfur such as suggested by Stern, E. (1), is then not necessary for the study of the kinetics of vulcanization. It has the disadvantage of introducing more variables such as the action of the solvent on the rubber and the effect of the solvent on the rate of reaction. This latter has been shown by Le Blanc, M. & Kroeger, M. (1), to be dependent on the dielectric constant of the solvent.

Considerable work has been done on the rate at which sulfur and rubber combine. The figures by Spence, D. & Young, J. (1), have shown that the rate of vulcanization is a constant and depends only on the temperature and amount of sulfur present, mixings containing accelerators not being mentioned. These authors show that there is no curvature to the line showing the change of combined sulfur with time until practically all of the sulfur has been used up. This is a peculiar case of a chemical reaction and needs explanation. If the rate at which the sulfur and the rubber combine is a function of the concentrations only, then a curve of the type shown by curve A in Fig. 1, would be obtained.



In this case ( $t$ ) is the time and ( $x$ ) the amount of any of the reagents used up. ( $x_1$ ) is the total amount present. A glance at curve B which is similar to those obtained by Spence & Young (*loc. cit.*), shows that there must be some secondary action going on which causes the specific rate of reaction at successive times to become greater than that called for by the chemical kinetics of dilute solutions. This means that an equation of the type

$$\frac{dx}{dt} = K \cdot C_s \cdot C_r,$$

where (x) and (t) have the same significance as above and ( $C_s$ ) and ( $C_r$ ) are the concentrations of sulfur and rubber respectively, cannot be applied directly to the process of vulcanization. This may be explained in three ways, all of which are plausible. The first way was suggested by Skellon, H. (1), and is based on the theory that rubber forms only one compound, i.e.  $(C_{10}H_{16}S_2)_n$  and that this may form polysulfides with the excess sulfur and that these polysulfides become catalysts. In this way an auto-catalytic process is set up. This theory is rather doubtful on account of the fact that the first premise, that the sulfur and rubber form only one compound which then swells or dissolves in the remainder of the rubber, cannot be accepted as true. The reasons for this were given under the discussion of the adsorption theory. A second explanation is that accelerators may be formed from the resins and proteins by reaction with sulfur. These products would probably contain an  $-SH$  group which under certain conditions can act as a very powerful accelerator. That the sulfur actually does form compounds with the resins and proteins has been shown by the author (*loc. cit.*). The third explanation has not as yet had any proof and is given tentatively. It is known that substances which exist in two degrees of polymerization are more active chemically in the lower state. It is also known that the action of heat on rubber is to depolymerize or better to disaggregate it, the two processes being somewhat similar. As the heating of the rubber continues it becomes more and more disaggregated and thus more reactive chemically. It is thus easy to see that in this way the increased rate of reaction between rubber and sulfur might be explained. The proof of this point will entail an enormous amount of work especially as it will be necessary to take into consideration the action of different types of accelerators, including the so-called ultra-accelerators. The Peachy process should also throw considerable light on this question. This process has one drawback, however, which may preclude its use and that is the fact that even with very thin strips it is impossible to obtain an absolutely uniform vulcanization throughout the piece. The surfaces are sure to be vulcanized to a greater extent than the interior.

From the foregoing discussion it is evident that there are several well established facts concerning vulcanization which might be correlated into a workable theory. These facts are as follows:

1. During vulcanization a chemical reaction takes place between the sulfur and the rubber.

2. During this reaction *all* of the rubber combines with some sulfur. This is obvious from the fact that *all* the rubber becomes progressively more difficultly soluble and vulcanized rubber cannot be fractionated by means of solvents.

3. The strength of vulcanized rubber depends, *for a given mixing*, on the amount of combined sulfur, the time and temperature of heating.

4. As vulcanization proceeds the strength of the rubber always increases to a maximum and then decreases.

5. The shorter the time and the lower the temperature necessary to obtain the optimum cure the greater is the strength of the vulcanized rubber.

6. Mixings of any given rubber which are made to vulcanize very rapidly by means of powerful accelerators always require less combined sulfur to reach the optimum cure, and the strength of the vulcanized sample at this cure is always greater than when the proper cure is obtained in a longer time. This is shown very well by the work of Cranor, D. F. (1).

7. When rubber is heated or milled it loses its strength and becomes softer and more plastic. It also dissolves more readily in the ordinary solvents. The rubber has become depolymerized or disaggregated.

8. Rubber dissolves sulfur and the solubility increases with rise in temperature until at the ordinary temperature of vulcanization ( $140^{\circ}$ ) it attains a value of about 20 parts per 100 of rubber. Venable, C. S. & Green, C. D. (1).

The action of accelerators is not mentioned specifically in the foregoing discussion because the function of these substances is to produce an active form of sulfur and the mechanism of the reactions by which this form is generated has no bearing on the behavior of the sulfur after the active form is produced. Some accelerators produce active sulfur more rapidly than others and naturally the rate of vulcanization will depend solely on the rate at which the active form of sulfur is produced. In the case of those accelerators which function at low temperatures the reaction between the sulfur and the accelerator proceeds at a fairly rapid rate even at ordinary temperatures and thus there is no fundamental difference between low and high temperature vulcanization. The Peachy process is merely a method of producing the active form of sulfur at ordinary temperatures.

Before discussing the facts just enumerated it will be best to consider briefly the rubber itself. Rubber is not a simple substance to which any definite chemical structure can be assigned. Its properties all indicate that it is a polyphase system, exclusive of the resins and proteins which always are present in the commercial material. All work up to the present has failed to separate any of these phases and the analyses all show that the ultimate composition is expressed by the empirical formula  $(C_5H_8)_n$ . This form is chosen in preference to  $(C_{10}H_{16})_n$  because there is no justification for the assumption that  $C_{10}H_{16}$  is the simplest formula which can be assigned to rubber. This formula was first proposed by C. O. Weber who considered rubber to be a terpene and later received support from the work of Harries at the time he proposed the cyclooctadien formula. This structure

of rubber is not accepted and until some more definite and plausible one is proposed it will probably be better to write the formula  $(C_5H_8)_n$ .

Rubber being a polyphase system, it must follow that although the different phases all have the same composition they are structurally different and not mutually soluble in all proportions. If the different "phases" were all mutually soluble in all proportions, we should have a single phase and not a polyphase system. This naturally complicates matters and a complete explanation of the mechanism will never be made until it is possible to separate the phases of rubber and establish their structures.

The action of heat and mechanical working on rubber results in a redistribution of the phases or in the disaggregation of the larger particles. In other words these treatments increase the dispersity of the rubber. If the action of the sulfur is a surface action, then an increase in the dispersity should result in a rubber which will add sulfur more rapidly, whereas if the sulfur is actually dissolved in the rubber, there should be little or no difference in the rate of reaction, for different degrees of dispersity. On the other hand if the heat and mechanical working actually cause a depolymerization in the chemical sense, then there would be more free double bonds and hence a larger effective concentration of the rubber which would result in a more rapid reaction with the sulfur, all other things being equal. Some contradictory data have been published on this point by Axelrod, P. (1) and Spence, D. & Ward, C. A. (1), and before any definite conclusions are drawn it will be necessary to check the work of these investigators very carefully. Considerable light will be thrown on the process of vulcanization when this point is finally cleared up.

It has been stated above in fact No. 1 that vulcanization is a chemical reaction between rubber and sulfur. Considering first a single phase of the system we know that it consists of several  $C_5H_8$  groups linked together in such a way that there is one double bond for each group. Each of these double bonds is capable of being saturated by sulfur. Provided we are dealing with the ultimate particle of this particular phase there will be no decomposition or disaggregation due to the heating. If we now saturate the double bonds successively we shall obtain a series of compounds with increasing sulfur contents until all of the double bonds have been saturated. It follows then that if we accept the chemical reaction as a fact we must also accept the formation of a series of sulfur-rubber compounds as first proposed by Weber. However, the Weber series will have to be modified to account for the polyphase structure of the rubber. It was stated in fact No. 2 that all of the rubber combined with some sulfur and hence every phase present in the system forms a series of compounds with sulfur. In this way we have, not a single series of sulfur addition products but several, and according to the size of the aggregate the percentage of combined sulfur in each phase will vary.



Thus it is easy to explain the fact that there are no sharp breaks in the sulfur addition curve.

When the mixture of rubber and sulfur is heated the rubber dissolves the sulfur and the chemical action follows. At the same time the rubber is being disaggregated by the action of the heat and this process goes on independently of the sulfur addition. The more the rubber is disaggregated the weaker it becomes and the degree of disaggregation depends only on the temperature and time of heating. Thus we have two actions going on simultaneously, the heat tending to decrease the strength and the sulfur addition tending to increase it. Several authorities assume that the sulfur acts as a polymerizing agent as well and in this way increases the strength of the rubber. It is necessary to make a distinction between polymerization and condensation. If the sulfur reacts on the rubber in such a way that two rubber molecules are joined together through the medium of sulfur atoms the process is one of condensation and not of polymerization. This assumption does not seem to be borne out by the facts that short cures or low temperature cures when fast accelerators are used require less total sulfur in the mixing and also less combined sulfur to reach their maximum strength and this maximum strength is always greater than the maximum of the longer cures. The action of the sulfur is not a simple one. In the first place the sulfur dissolved in the rubber is probably present as  $S_8$ . If we assume that in butyl alcohol the sulfur is present as  $S_8$ , then the sulfur in the rubber has the same molecular weight because as the author has shown in the paper read at the New Haven Meeting already referred to, the ratio of the concentration of the sulfur in rubber and butyl alcohol is a constant up to the saturation point. Sulfur cannot add on to the rubber as  $S_8$  but must first be reduced to the atomic form. This reduction is probably accomplished in part by the rubber itself and for the rest by the reaction with the resins and proteins which are present. The rate at which this active sulfur combines with the rubber depends on the rate at which it is formed. If it is formed slowly the action of the heat on the rubber itself is more pronounced and the rubber is disaggregated. If the action is fast the effect of the heat is less and the result is a stronger product. We can now assume that every particle of rubber independent of its size requires a certain number of sulfur atoms to give it the best physical properties. For the sake of simplicity let us assume that two atoms of sulfur is the required amount. If only one atom is added the sample is undercured and if three are added it is overcured. If the reaction producing the active sulfur is slow there will be a greater number of smaller particles of rubber to be satisfied and hence the percentage of combined sulfur will be greater. When the reaction is very fast the effect of heat is very slight and a well vulcanized sample is obtained with a smaller percentage of combined sulfur. This leads

directly to the statement that for every degree of aggregation of rubber there is a certain amount of sulfur which when combined with the rubber will impart to it its maximum physical properties. The degree of aggregation in this sense means the average size of the particle. Thus it is easy to explain overcuring and undercuring. Suppose now that most of the particles of rubber have their quota (the assumed two atoms) of sulfur and the heating is continued. The vulcanized particle may then split into two smaller particles each having one atom of sulfur or one having two and the other more. In either case the sample would show the characteristics of an undercured piece and this is exactly what happens in cases of reversion. The further addition of sulfur would then result in a second increase in the strength of the rubber. This phenomenon has been described by Twiss, D. F. (12), in the case of some mixings and the above is a plausible explanation.

The disaggregating action of heat on the vulcanized rubber is probably slower than on the unvulcanized and for that reason the action of the sulfur can assert itself in time to keep the rubber from disaggregating completely. Some accelerators when used in certain proportions give a mixing in which the strength remains fairly constant over long periods of vulcanizing. This is easily explained on the same basis if the rate of decrease in strength due to the heat is equal to the rate of increase due to the addition of the sulfur.

In the case of mixings which vulcanize at low temperatures we should naturally expect a stronger product as the effect of the heat is less and this is exactly what does happen as Cranor, D. F. (1), has shown.

### *Recapitulation:*

The process of vulcanization consists in the addition of sulfur to the rubber aggregate while the latter is being degenerated by heat in the case of hot cures. The more rapidly the sulfur is added the less the disaggregation and the greater the strength. Every degree of aggregation requires a definite amount of sulfur to bring out the best physical properties of the rubber.

This explanation seems to cover all the facts known about vulcanization in a fairly comprehensive manner.



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*F.P.* 470,833 (1913); *J.S.C.I.* **34**, 188 (1915); *Kunst.* **12**, 126 (1922).
- Baudrimont.**
- On the alteration of tubes of vulcanized rubber in iodine solutions.  
*J. Pharm.* **17**, (4) 218 (1873).

**Baumetz, M.**

1. Action of iodine on rubber.  
Chem. News 28, 110 (1873).

**Baumhauer, E. H. von.**

1. On the elementary composition of gutta percha.  
J. Prakt. Chem. 78, 277 (1859);  
Centr. (1860) p. 186 & 335; Jahresb.  
ber. (1859) p. 518; See Gmelin (1)  
p. 339.

**Bayer & Co.**

1. Ammonia, aliphatic amines or alkalies as preventatives against the deterioration of synthetic rubber.  
D.R.P. 257,813 (1911); Chem. Ind. 36, 214 (1913); Chem. Tech. Report. 37, 211 (1913); Jahresb. Chem. Tech. 59, II, 569 (1913); See Ditmar (64).  
E.P. 29,213 (1911); I.R.J. 43, 207 (1912); Chem. Tech. Report. 36, 609 (1912); J.S.C.I. 31, 829 (1912); Chem. Zt. 36, 720 & 825 (1912).
2. Bayer patent accelerator.  
I.R.J. 48, 325 (1914); See Bayer & Co. (5).
3. Prevention of oxidation and resinification of synthetic rubber.  
D.R.P. 264,820 (1911); Jahresb. Chem. Tech. 59, II, 569 (1911).  
D.R.P. 266,153 (1912) Add. to 264,820 (1911); Chem. Tech. Report. 37, 644 (1913); C.A. 8, 586 (1914); Chem. Ind. 36, 729 (1913); See Fonrobert & Harries (1) p. 141.  
U.S.P. 1,039,741 (1912); J.S.C.I. 31, 1043 (1912); See Hemming (1) p. 164.  
F.P. 441,477 (1912); J.S.C.I. 31, 829 (1912).
4. Preparation of a rubber-like substance.  
D.R.P. 254,548 (1910); Chem. Ind. 36, 26 (1913); Genussm. 28, 58 (1914); Jahresb. Chem. Tech. 58, II, 586 (1912); See Ditmar (64).  
E.P. 1,124 (1911); Chem. Tech. Report. 36, 175 (1912); C.A. 6, 1858 (1912); J.S.C.I. 31, 141 (1912).  
F.P. 435,076 (1911); J.S.C.I. 31, 292 (1912).
5. Piperidine and its homologues.  
D.R.P. 265,221 (1912); Chem. Ind. 36, 693 (1913); Angew. 26, II, 678 (1913); Jahresb. Chem. Tech. 59, II, 574 (1913); C.A. 8, 435

(1914); Chem. Tech. Report. 37, 604 (1913); Centr. 1913, II, 1444.  
F.P. 464,533 (1913); J.S.C.I. 33, 493 & 839 (1914); 34, 725 (1915); Kunst. 10, 126 (1920); Caout. 12, 8693 (1915).  
E.P. 11,530 (1913); J.S.C.I. 32, 1078 (1913); C.A. 8, 3635 (1914); I.R.J. 46, 14, 958 & 1108 (1913); 50, 501 (1915); Caout. 14, 9347 (1917); 16, 9783 (1919).  
Aust. P. 66,713 (1914); Kunst. 9, 144 (1922).  
Aust. P. 67,833 (1914); Kunst. 9, 143 (1922).  
Aust. P. 67,834 (1914); Kunst. 9, 143 (1922).

## 6. Derivatives of piperidine and its homologues.

D.R.P. 266,619 (1912) Add. to 265,221; Centr. 1913, II, 1834; Jahresb. Chem. Tech. 59, II, 574 (1913); J.S.C.I. 33, 94 (1914); Angew. 27, II, 5 (1914); 26, II, 678 (1913); Chem. Tech. Report. 37, 666 (1913); Chem. Ind. 36, 729 (1913).  
F.P. 464,533 (1914); Caout. 17, 10259 (1920).  
E.P. 11,209 (1913); C.A. 8, 3508 (1914).  
E.P. 11,615 (1913) Add. to 11,530; C.A. 8, 3635 (1914); J.S.C.I. 33, 326 (1914); I.R.J. 47, 466 & 513 (1914); Kunst. 4, 360 (1914); Caout. 14, 9347 (1917); 16, 9783 (1919); Chem. Tech. Report. 38, 257 (1914).  
U.S.P. 1,126,469 (1915); C.A. 9, 732 (1915); J.S.C.I. 34, 291 (1915); Chem. Tech. Report. 38, 257 (1914).  
Aust. P. 66,174 (1914) Add. to 66,173; Kunst. 9, 144 (1922).  
Aust. P. 67,835 (1914); Kunst. 9, 144 (1922).  
Belg. P. 261,724; Kunst. 4, 393 (1914).

## 7. Piperidine and homologues for hard rubber.

D.R.P. 266,618 (1912) Add. to 255,680; Centr. 1913, II, 1834; C.A. 8, 1022 (1914); Chem. Tech. Report. 37, 667 (1913); Jahresb. Chem. Tech. 59, II, 573 (1913); Chem. Ind. 36, 78 (1913).  
F.P. 18,428 (1913) Add. to 456,598; C.A. 9, 1860 (1915); Kunst. 4, 238 (1914).

8. Synthetic rubber with piperidine or its homologues cured for a short time at low temperatures.  
D.R.P. 267,945 (1912) Add. to 266,-618; *Kunst.* 4, 75 (1914); *Centr.* 1914, I, 206; *C.A.* 8, 1878 (1914); *Chem. Tech. Report.* 38, 41 (1914); *Jahresb. Chem. Tech.* 59, II, 574 (1913); *J.S.C.I.* 33, 93 (1914).
9. Piperidine and homologues with synthetic rubber.  
D.R.P. 268,387 (1912) Add. to 266,-618; *J.S.C.I.* 33, 269 (1914); *C.A.* 8, 1879 (1914); *Jahresb. Chem. Tech.* 59, II, 574 (1913); *Kunst.* 4, 75 (1914); *Chem. Tech. Report.* 38, 41 (1914).  
*Belg. P.* 261,870; *Kunst.* 4, 393 (1914).
10. Colored caoutchouc substances.  
*E.P.* 17,830 (1912); *C.A.* 8, 434 (1914); *J.S.C.I.* 32, 919 (1913).  
*U.S.P.* 1,113,614 (1914); See K. Gottlob (6).
11. Tannic acid as a preservative for synthetic rubber.  
D.R.P. 259,722 (1912) Add. to 250,920; *Chem. Tech. Report.* 37, 360 (1913); See Ditmar (64).  
*F.P.* 16,938 (1912) Add. to 441,-655; *Chem. Tech. Report.* 37, 642 (1913); *J.S.C.I.* 31, 888 (1912); 32, 667 (1913); *Chem. Ind.* 36, 365 (1913).  
*E.P.* 28,821 (1912); *J.S.C.I.* 32, 1023 (1913).
12. Coloration of rubber.  
*F.P.* 450,567 (1912); *Chem. Tech. Report.* 37, 359 (1913); *J.S.C.I.* 32, 615 (1913).
13. Vulcanizing synthetic caoutchouc with accelerators.  
D.R.P. 268,947 (1913) Add. to 266,-618; *C.A.* 8, 2073 (1914); *J.S.C.I.* 33, 365 (1914); *Centr.* 1914, I, 510; *Jahresb. Chem. Tech.* 60, II, 451 (1914); *Chem. Tech. Report.* 38, 79 (1914).  
*E.P.* 11,530 (1913); *J.S.C.I.* 32, 1078 (1913); *Caout.* 12, 8660 (1914).
14. Difficultly volatile bases and derivatives or difficultly volatile derivatives of easily volatile bases as accelerators.  
D.R.P. 269,512 (1913) Add. to 265,-221; *C.A.* 8, 2073 (1914); *Jahresb. Chem. Tech.* 60, II, 445 (1914); *J.S.C.I.* 33, 365 (1914); *Angew.* 27, II, 179 (1914); *Chem. Tech. Report.* 38, 79 (1914); See Gottlob (6) p. 115.  
*E.P.* 12,777 (1913); *C.A.* 8, 3723 (1914); *Kunst.* 4, 347 (1914); *J.S.C.I.* 33, 758 (1914); *I.R.J.* 48, 272 (1914); *Caout.* 14, 9348 (1917); 16, 9783 (1919).  
*U.S.P.* 1,130,903 (1915) *Synthetic Patents Co.*; *C.A.* 9, 1135 (1915); *J.S.C.I.* 34, 437 (1915); *Centr.* 1914, I, 594.  
*F.P.* 18,705 (1913) Add. to 464,533; *C.A.* 9, 2164 (1915).  
*Aust. P.* 68,724 (1914) Add. to 66,-173; *R. Age.* 7, 110 (1920); *Kunst.* 9, 144 (1922).  
*Aust. P.* 67,836 (1914); *R. Age.* 7, 110 (1920); *Kunst.* 9, 144 (1922).  
*Belg. P.* 262, 299.
15. Vulcanizing synthetic rubber. (Hofmann & Delbruck).  
D.R.P. 255,680 (1911); *Chem. Tech. Report.* 37, 68 (1913).  
D.R.P. 250,920 (1911); *Chem. Tech. Report.* 36, 545 (1912); *Jahresb. Chem. Tech.* 58, II, 586 (1912).  
*F.P.* 446,598 (1912); *J.S.C.I.* 32, 152 (1913).  
*U.S.P.* 1,081,613 (1913).  
*U.S.P.* 1,081,614 (1913); *J.S.C.I.* 33, 94 (1914).  
*E.P.* 2,312 (1912); *J.S.C.I.* 31, 651 (1912); *Chem. Tech. Report.* 36, 422 (1912).  
*E.P.* 2,313 (1912); *C.A.* 7, 2487 (1913); *J.S.C.I.* 31, 547 (1912); *Chem. Tech. Report.* 36, 422 (1912).  
*E.P.* 24,637 (1912) Add. to 2,313; *J.S.C.I.* 32, 706 (1913).
16. Use of tannin in synthetic rubber. (Delbruck & Meisenberg).  
*U.S.P.* 1,076,196 (1913).
17. Reaction products of ozone on rubber. (Hofmann, Coutelle, Delbruck & Meisenberg).  
*U.S.P.* 1,084,335 (1913).  
*U.S.P.* 1,084,336 (1913).  
*U.S.P.* 1,084,338 (1913); *C.A.* 8, 1020 (1914).
18. Same title. (Hofmann & Coutelle).  
*U.S.P.* 1,084,337 (1913); *C.A.* 8, 1020 (1914).

19. Accelerators having a dissociation constant greater than  $1 \times 10^{-8}$ . (Hofmann & Gottlob).  
D.R.P. 280,198 (1914); *Jahresb. Chem. Tech.* 60, II, 455 (1914); *Kunst.* 4, 369 (1914); *J.S.C.I.* 34, 436 (1915); *Angew.* 27, II, 732 (1914); *Gummi. Zt.* 29, 217 (1915); *C.A.* 9, 1408 (1915); *Caout.* 13, 8836 (1916); *Centr.* 1914, II, 1371; *Chem. Tech. Repert.* 38, 573 (1914).  
U.S.P. 1,149,580 (1915) *Synthetic Patents Co.*; *I.R.W.* 52, 648 (1915); *J.S.C.I.* 34, 971 (1915).  
E.P. 12,661 (1914); *I.R.W.* 53, 115 (1915); *C.A.* 10, 132 (1916); *J.S.C.I.* 34, 1062 (1915); *Gummi. Zt.* 30, 253 (1915); *Kunst.* 12, 6 & 29 (1922); *Caout.* 16, 9783 (1919).  
F.P. 19,455 (1915) *Add. to 464,533*; *Chem. Tech. Ubers.* 43, 235 (1919); *J.S.C.I.* 34, 725 (1915).  
Aust. P. 69,974 (1915) *Add. to 66,173*; *Kunst.* 9, 144 (1922); 12, 126 (1922).
20. Preparation of aldehyde ammonia.  
D.R.P. 290,808 (1914); *J.S.C.I.* 35, 617 (1916); *Chem. Tech. Repert.* 40, 148 (1916).
21. Urea as a polymerizing agent for synthetic rubber. (Hofmann & Consem).  
U.S.P. 1,113,630 (1914); *J.S.C.I.* 33, 1100 (1914).
22. Accelerator.  
*Ital. P.* 139,536 (1914); *Ann. Chim. Appl.* 1, 376 (1914).
23. See Ditmar (60).
24. Elastifiers for synthetic rubber.  
D.R.P. 301,757 (1915); *I.R.J.* 60, 1289 (1920); *Kunst.* 10, 222 (1920); *J.S.C.I.* 39, 757a (1920); *Gummi. Zt.* 35, 225 (1920); *Caout.* 18, 11027 (1921); *Chem. Tech. Ubers.* 45, 231 (1921); *Jahresb. Chem. Tech.* 66, II, 387 (1920).  
Aust. Pat. 87,577 (1917); *Kunst.* 13, 44 (1923).
26. Bayer patents used by the North British Rubber Co.  
*I.R.J.* 52, 853 (1916); *C.A.* 11, 547 (1917).
27. Compounding materials for rubber.  
D.R.P. 303,224 (1916); *Chem. Tech. Ubers.* 46, 59 (1922); *J.S.C.I.* 40, 269, (1921).
28. Prevention of deterioration of balloon fabrics.  
D.R.P. 303,966 (1916); *Centr.* 1919, IV, 968; *Kolloid Z.* 27, 324 (1920).
29. Process for production of piperidine-piperidyl-dithio-carbamic acid.  
D.R.P. 316,009 (1917); *J.S.C.I.* 39, 386a (1920); *I.R.W.* 62, 656 (1920); *Centr.* 1920, II, 243; *Kolloid Z.* 27, 316 (1920).
30. Bayer patents used by the Hooley Hill Rubber & Chemical Co.  
*I.R.J.* 53, 207 (1917).
31. Use of weak accelerators in large amounts.  
D.R.P. 303,984 (1917); *Kunst.* 10, 158 (1920); *Gummi. Zt.* 34, 839 (1920); *I.R.W.* 63, 254 (1921); *C.A.* 15, 2214 (1921); *Centr.* 1920, IV, 412; *Chem. Tech. Ubers.* 45, 71 (1921); *Chim. & Ind.* 6, 85 (1921); *Jahresb. Chem. Tech.* 66, II, 388 (1920).  
Aust. P. 87,336 (1922); *Centr.* 1922, IV, 896; *Kunst.* 13, 44 (1923).
32. Aniline sulfate as an accelerator.  
D.R.P. 305,667 (1917); *Chem. Tech. Ubers.* 45, 71 (1921); *Kunst.* 10, 215 (1920); *Gummi. Zt.* 34, 908 (1920); 36, 28 (1921); *I.R.W.* 63, 254 (1921); *C.A.* 15, 2214 (1921); *Centr.* 1920, IV, 412.  
Aust. P. 1,429; *R. Age* 10, 167 (1921); *Gummi. Zt.* 36, 28 (1921); *Chim. & Ind.* 6, 85 (1921); *Jahresb. Chem. Tech.* 66, II, 388 (1920).  
Aust. P. 87,578 (1922); *Centr.* 1922, IV, 896; *Kunst.* 13, 44 (1923).
33. Soft elastic vulcanizates of greater strength and elongation.  
D.R.P. 326,819 (1917); *I.R.W.* 64, 661 (1921); *Gummi. Zt.* 35, 116 (1920); *J.S.C.I.* 40, 188a (1921); *Centr.* 1921, II, 133; *Kolloid Z.* 29, 154 (1921); *Caout.* 18, 11028 & 11147 (1921); *Chem. Tech. Ubers.* 46, 18 (1922); *Jahresb. Chem. Tech.* 66, II, 390 (1920).  
Aust. P. 82,089; *Kunst.* 12, 149 (1921).
34. Metallic oxides and superoxides as accelerators with amines.  
D.R.P. 328,610 (1917); *J.S.C.I.* 40, 229a (1921); *Chem. Tech. Ubers.* 46, 59 (1922); *I.R.J.* 60,

- 1289 (1920); I.R.W. 64, 741 (1921); Kunst. 11, 15 (1921); Centr. 1921, II, 181; Kolloid Z. 29, 154 (1921); Jahresh. Chem. Tech. 66, II, 390 (1920); Gummi. Zt. 36, 28 (1921).  
Aust. P. Appl. 1,430 (1918); Gummi. Zt. 36, 28 (1921); I.R.J. 60, 1267 (1920).  
Aust. P. 87,469 (1918); Kunst. 13, 44 (1923).
35. Use of amines, aniline sulfate and metallic oxides or peroxides in rubber compounds.  
D.R.P. 345,160 (1917); I.R.W. 66, 680 (1922); I.R.W. 65, 276 (1921); 66, 680 (1922); J.S.C.I. 47, 224a (1922); Centr. 1922, II, 396; Gummi. Zt. 36, 462 (1922).
36. License of Bayer patents to Alfred Smith of Clayton, Manchester.  
Caout. 15, 9514 (1918).
37. Use of vulcanization accelerators in the preparation of sulfurated oils. (Factis).  
D.R.P. 354,172 (1920); Gummi. Zt. 36, 1123 (1922); Centr. 1922, IV, 592; Caout. 19, 11605 (1922); Kunst. 12, 176 (1922).
38. Increasing the elasticity of vulcanized rubber.  
D.R.P. 332,347 (1921); Gummi. Zt. 35, 567 (1921); Kunst. 11, 87 (1921); R. Age 10, 370 (1922); Caout. 18, 11103 (1921); Chem. Tech. Übers. 46, 105 (1922); Chim. & Ind. 6, 645 (1921); I.R.W. 63, 339 (1921); I.R.J. 61, 599 (1921); J.S.C.I. 40, 359a (1921).
39. Hydroxy or nitro compounds in synthetic rubber to retard oxidation.  
D.R.P. 33,496 Add. to 329,676; R. Age 11, 347 (1922).
40. Lessening the tackiness of synthetic and natural rubber.  
D.R.P. 43,563 (1922); Kunst. 12, 136 (1922).
41. Prevention of tackiness and resinification of natural and synthetic rubbers.  
D.R.P. 366,114 (1922); Chem. Zt. 46, 1052 (1922); Kunst. 13, 34 & 70 (1923); Gummi. Zt. 37, 597 (1923); J.S.C.I. 42, 616a (1923).
42. Preparation of a rubber substitute of practical value.  
D.R.P. 256,413 (1911); Add. to 250,920; Chem. Tech. Repert. 37, 158 (1913); Chem. Ind. 36, 142 (1913).
- Bayles, E. A.**  
1. Vulcanization of electric cable covers.  
E.P. 114,373 (1918) British Insulated & Helsby Cables, Ltd; I.R.W. 58, 599 (1918).
- Beadle, C. & Stevens, H. P.**  
1. Vulcanization tests with plantation rubber.  
Chem. News 96, 37, 187 & 235 (1907); 98, 187 & 235 (1908); 99, 249 (1909); Analyst 32, 337 (1908); 33, 26 (1908); J.S.C.I. 26, 1245 (1907); Chem. Eng. (Phila.) 6, 212 & 266; 7, 16 (1907); Centr. 1907, I, 778; 1907, II, 1665 & 1908; C.A. 1, 713 & 2749 (1907); 2, 713 (1908); I.R.J. 34, 211 & 760 (1907); Jahresh. Chem. Tech. 54, II, 537 (1908); Gummi. Zt. 21, 1182 (1907); 22, 439 (1908).
2. The so-called "nerve" of rubber.  
Chem. News 96, 247 (1907); 97, 73 (1908); Gummi. Zt. 22, 633 (1908) Centr. 1908, I, 497 & 2062; C.A. 2, 713 (1908); J.S.C.I. 26, 1287 (1907); See Fonrobert & Harries (1) p. 47.
3. The acid content of crude rubber.  
I.R.J. 41, 1257 (1910); Gummi. Zt. 25, 1530 (1911); J.S.C.I. 30, 757 (1911); C.A. 6, 1541 (1912).
4. The influence of mineral ingredients on the properties of rubber.  
J.S.C.I. 30, 1421 (1911); 31, 95 (1912); Genussm. 23, 630 (1913); Kolloid Z. 11, 79 (1912); I.R.J. 43, 79 & 130 (1912); C.A. 6, 807 (1912); Angew. 25, 1496 (1912); Caout. 9, 5941 & 6027 (1912); Centr. 1912, I, 1159; Jahresh. Chem. Tech. 58, II, 598 (1912); Chem. Zt. 36, 220 (1912); Chem. Tech. Repert. 36, 306 & 420 (1912); Gummi. Markt. 6, 171 (1912); See Gottlob (6) p. 67 & 70; Porritt (1) p. 46.
5. Some analyses of Hevea latex.  
Analyst 36, 6 (1911); Genussm. 23, 426 (1912); C.A. 5, 2338 (1911); J.S.C.I. 30, 141 (1911); I.R.J. 41, 216 (1911); Gummi. Zt. 25, 753 (1911).
6. Crude rubber and its valuation.  
I.R.J. 41, 1399 (1911); Gummi. Zt.

- 25, 1882 (1911); C.A. 6, 1375 (1912); Chem. Trade J. 48, 554 (1911).
7. Note on the effect of reworking typical para rubbers.  
J.S.C.I. 30, 1425 (1911); C.A. 6, 807 (1912).
8. The nature of the resinous constituent and its influence on the quality of the rubber.  
8th Int'l. Cong. Appl. Chem. 25, 581 (1912); Gummi.Zt. 27, 907 (1913); Caout. 13, 8825 & 9038 (1916); C.A. 7, 4085 (1913); See Gottlob (6) p. 115; (11) part 2, p. 48.
9. The so-called insoluble constituents of rubber and their influence on the quality of the same.  
J.S.C.I. 31, 999 (1912); Kolloid Z. 11, 61 (1912); I.R.J. 44, 554 & 603 (1912); C.A. 7, 270 (1913); J.C.S. 102, i, 789 (1912); J.C.S. Ann. Repts. 9, 78 (1912); Gummi.Zt. 27, 9 (1912); Chem. Tech. Repert. 37, 19 (1913); Genusssm. 32, 548 (1916); See Gottlob (6) p. 50 & 115; Zimmerman (1) p. 268; Porritt (1) p. 7 & 46; Dubosc & Luttringer (1) p. 166.
10. The nitrogenous constituent of para rubber and its bearing on the nature of synthetic rubber.  
J.S.C.I. 31, 1099 & 1103 (1912); J.C.S. 104, i, 190 (1913); C.A. 7, 905 (1913); I.R.J. 45, 168 (1913); Gummi.Zt. 27, 965 (1913); Chem. News 106, 243 (1912); Mon. sci. 80, (5) 115 (1914); Genusssm. 28, 52 (1914); Bull. Imp. Inst. 11, 161 (1913); See Porritt (1) p. 7 & 46.
11. Method for determining the amount of insoluble particles in raw rubber.  
Analyst 37, 13 (1912); I.R.J. 43, 193 (1912); C.A. 6, 808 (1912).
12. The insoluble constituents of Ceara & Rambong rubber.  
Kolloid Z. 12, 46 (1913); I.R.J. 45, 313 & 345 (1913); Centr. 1913, I, 1796; Chem. Tech. Repert. 37, 401 (1913); J.S.C.I. 32, 203 (1913); Jahresb. Chem. Tech. 59, II, 578 (1913); Bull. Imp. Inst. 11, 351 (1913); See Gottlob (6) p. 50 & 115.
13. An investigation into the nature and properties of Hevea latex.  
8th Int'l. Cong. Appl. Chem. 9, 17 (1912); C.A. 6, 3196 (1912); Centr. 1913, II, 2141; Kolloid Z. 13, 207 (1913); Chem. Zt. 36, 1271 (1912); J.S.C.I. 31, 887 (1912); See Gottlob (6) p. 51; deVries (24) p. 24.
14. The viscosity of rubber solutions.  
I.R.J. 45, 1081 (1913); 45, 529 (1914); C.A. 7, 3548 (1913); I.R.R. Oct. (1914) p. 574; Chemical World 3, 224 (1914).
15. Production of rubber of uniform color  
J.S.C.I. 34, 1104 (1915); C.A. 10, 1610 (1916); Caout. 12, 8730 (1915) 13, 9032 (1916); Rubber Recueil (1914) p. 357.
16. Alkali treatment of rubber coagulum.  
J.S.C.I. 35, 643 (1916); I.R.J. 51, 713 (1916); C.A. 10, 3000 (1916); Caout. 14, 9152 (1917).
17. Some considerations regarding latex formation.  
Chem. World 1, 261 & 370 (1912).
18. On the addition of vinegar for coagulation and other coagulation methods.  
Pub. N. I. Landbouw Syndicate 7th year (1915) Af. 1, p. 19.
- Beadle, C., Stevens, H. P. & Morgan, S.**
1. Sodium bisulfite in the manufacture of plantation rubber.  
I.R.J. 46, 222 (1913); J.S.C.I. 32, 835 (1913); C.A. 7, 3670 (1913); Bull. Imp. Inst. 12, 133 (1914); See deVries (24) p. 97; Gottlob (11) part 2, p. 47.
- Beale & Enderby.**
1. Dry distillation of rubber.  
Bull. Soc. d'Encouragement (1834) p. 330; Jahresber. (1836) p. 320; Inst. (1834) No. 69, p. 290; Berz, Jahresber. 15, 320 (1836); See Gmelin (1) 17, 343 (1866); Tassily (1) p. 306.
- Bean, P. L.**
1. Supposed retarding effect of dimethylamine dimethyldithio-carbamate.  
I.R.J. 63, 354 (1922); J.S.C.I. 41, 261a (1922); Centr. 1922, II, 883; I.R.W. 66, 680 (1922); C.A. 16, 1886 (1922).
2. Effect of litharge on accelerators of the vulcanization of rubber.  
I.R.J. 64, 1051 (1922); J.S.C.I. 42, 106a (1923); I.R.W. 67, 360 (1923).

**Beaver, C. J. & Claremont, E. A.**

1. Artificial ageing of rubber sheet.  
E.P. 23,727 (1910); J.S.C.I. 30,  
1323 (1911); C.A. 6, 1542 (1912);  
See Hemming (1) p. 159.

**Becker, R.**

1. Yearly report for 1909 on the chemistry of rubber and gutta percha.  
Gummi. Zt. 24, 782, 817 & 893 (1910).
2. Concerning the caoutchouc tetrabromide of Hübener.  
Gummi. Zt. 25, 531, 598 & 677 (1911); Genusssm. 24, 537 & 718 (1912); Chem. Tech. Report. 35, 260 (1911); J.S.C.I. 30, 142 (1911); C.A. 5, 3518 (1911).
3. The bromide determination of rubber according to Hübener.  
Gummi. Zt. 26, 1503 (1912); Chem. Tech. Report. 36, 584 (1912); J.S.C.I. 31, 693 (1912); C.A. 6, 2545 (1912); Genusssm. 26, 266 (1913); 32, 547 (1916).

**Bedford, C. W.**

1. Sulfur reaction products of accelerators.  
E.P. 130,857 (1919) North British Rubber Co; I.R.W. 61, 80 (1919); I.R.J. 58, 477 (1919); C.A. 14, 235 (1920); Gummi. Zt. 34, 78 (1919); J.S.C.I. 38, 731a (1919); J.S.C.I. Ann. Repts. 4, 334 (1919); Kunst. 12, 30 (1922); Caout. 17, 10157 & 10288 (1920).  
Can. P. 201,177 (1920) Goodyear Tire & R. Co; I.R.W. 62, 733 (1920).  
U.S.P. 1,371,662 (1921);  
U.S.P. 1,371,663 (1921);  
U.S.P. 1,371,664 (1921); I.R.W. 64, 581 (1921); J.S.C.I. 40, 312a (1921); Gummi. Zt. 35, 784 (1921); C.A. 15, 1832 (1921); Centr. 1921, IV, 47; Centr. 1921, IV, 46. See Hemming (1) p. 160.  
F.P. 492,140 (1922); Kunst. 12, 127 (1922).
2. Method of compounding accelerators.  
U.S.P. 1,380,765 (1921); J.S.C.I. 40, 554a (1921); I.R.W. 64, 819 (1921); C.A. 15, 3414 (1921); Centr. 1921, IV, 1038.
3. Hydrolyzed proteins as accelerators.  
U.S.P. 1,323,951 (1919); Goodyear

Tire & R. Co; Mon. sci. 12, (5) 5 Brevets; C.A. 14, 368 (1920); J.S.C.I. 39, 123a (1920); Gummi. Zt. 34, 362 (1920); I.R.W. 61, 291 (1920).

E.P. 146,992 (1920); C.A. 14, 3826 (1920); I.R.W. 63, 173 (1921); Gummi. Zt. 36, 147 (1921); Kunst. 12, 31 (1922); J.S.C.I. 40, 440a (1921); I.R.J. 62, 525 (1921); Centr. 1921, IV, 430.

Can. P. 207,719 (1921); I.R.W. 63, 431 (1921).

F.P. 520,330 (1921); Chim. & Ind. 7, 749 (1922); R. Age 11, 240 (1922); Centr. 1921, IV, 812 & 1038; R. Age (London) 4, 240 (1922); Gummi. Zt. 37, 225 (1923).

4. Sulfur reaction product of methylene diphenyldiamine as an accelerator.

U.S.P. 1,418,772 (1922); Chim. & Ind. 27, 513 (1922); Centr. 1922, IV, 1176; Chem. Tech. Übers. 47, 14 (1923); I.R.W. 66, 745 (1922); Chem. Met. Eng. 27, 513 (1922); C.A. 16, 2794 (1922).

Can. Pat. 228,873 (1923); I.R.W. 68, 500 (1923).

5. Reclaiming vulcanized rubber containing protein.

U.S.P. 1,321,501 (1919) Goodyear Tire & R. Co.; J.S.C.I. 39, 35a (1920); C.A. 14, 234 (1920).  
F.P. 520,329 (1920); Kunst. 12, 152 (1922).

6. The chemistry of rubber vulcanization and acceleration.

J.I.E.C. 14, 856 (1922); Centr. 1922, IV, 1106; R. Age 12, 168 (1922); R. Age (London) 4, 46 (1923); Gummi. Zt. 37, 370 (1923).

**Bedford, C. W. & Gray, H.**

1. Reactions of accelerators during vulcanization. V. Dithiocarbamates, thiuram disulfides, and the action of hydrogen sulfide. (Abstract only. Original did not appear in 1922.)  
I.R.J. 64, 476 & 604 (1922).

**Bedford, C. W. & Kelly, W. J.**

1. Halogenated rubber.

U.S.P. 1,377,152 (1921) Goodyear Tire & R. Co; I.R.W. 64, 740 (1921); J.S.C.I. 41, 475a (1922); C.A. 15, 2749 (1921); See Hemming (1) p. 160.



**Bedford, C. W. & Scott, W.**

See Scott &amp; Bedford.

1. Reactions of accelerators during vulcanization.

J.I.E.C. *12*, 31 (1920); Gummi.Zt. *34*, 498 (1920); C.A. *14*, 866 (1920); I.R.W. *59*, 277 (1920); I.R.W. *61*, 206 (1920); Caout. *17*, 10372 (1920); J.S.C.I. *39*, 199a (1920); Centr. 1920, II, 603; 1920, IV, 18; Kunst. *10*, 141 & 211 (1920).

**Bedford, C. W. & Sebrell, L. B.**

1. Reactions of accelerators during vulcanization. III. Carbosulphydryl accelerators and the action of zinc oxide.

J.I.E.C. *13*, 1034 (1921); I.R.W. *65*, 356 (1922); J.S.C.I. *41*, 110a (1922); C.A. *16*, 176 (1922); Caout. *18*, 10985 (1921); Centr. 1921, IV, 429; 1922, II, 268; See Schidrowitz (32).

2. Reactions of accelerators during vulcanization. IV. Mechanism of the action of zinc compounds.

J.I.E.C. *14*, 25 (1922); Caout. *18*, 11127 (1921); *19*, 11275 & 11313 (1922); Gummi.Zt. *36*, 764 (1922); Centr. 1922, II, 883; J.S.C.I. *41*, 262a (1922); C.A. *16*, 855 (1922); See Schidrowitz (35).

**Bedford, C. W. & Sibley, R. L.**

1. Manufacture of thioureas.

U.S.P. 1,406,719 (1922) Goodyear Tire & R. Co; Chem. Zt. *46*, 370 (1922); Centr. 1922, II, 883; I.R.W. *66*, 493 (1922); Caout. *19*, 11561 (1922); C.A. *16*, 1681 (1922); Gummi.Zt. *36*, 869 (1922). Can. P. 207,983 (1921); I.R.W. *63*, 431 (1921). Can. P. 224,110 (1922); I.R.W. *67*, 88 (1922); C.A. *16*, 4365 (1922).

2. Reduced nitroso compounds as accelerators.

U.S.P. 1,406,717 (1922) Goodyear Tire & R. Co; Centr. 1922, II, 883 & 1223; Chem. Tech. Übers. *46*, 201 (1922); Chem. Zt. *46*, 370 (1922); I.R.W. *66*, 493 (1922); C.A. *16*, 1681 (1922); Gummi.Zt. *36*, 869 (1922); R. Age *11*, 12 & 314 (1922); Caout. *19*, 11561 (1922); See Schidrowitz (36). Can. P. 207,982 (1921); I.R.W. *63*, 431 (1921).

E.P. 173,545 (1922); I.R.W. *66*, 549 (1922); J.S.C.I. *41*, 149a (1922); C.A. *16*, 1682 (1922); Kunst. *13*, 9 (1923); I.R.J. *63*, 293 (1922); Centr. 1922, II, 884; Caout. *19*, 11527 (1922). U.S.P. 1,418,771 (1922); Gummi.Zt. *36*, 1370 (1922); I.R.W. *66*, 745 (1922); Centr. 1922, II, 884; 1922, IV, 639; Chim. & Ind. *27*, 706 (1922); Chem. Met. Eng. *27*, 705 (1922); C.A. *16*, 2794 (1922). F.P. 520,332 (1920); Kunst. *12*, 152 (1922); Chim. & Ind. *7*, 749 (1922); Centr. 1921, IV, 812.

3. Thioureas from reduced nitroso compounds.

U.S.P. 1,406,718 (1922) Goodyear Tire & R. Co; Centr. 1922, II, 883 & 1223; Chem. Zt. *46*, 370 (1922); I.R.W. *66*, 493 (1922); Caout. *19*, 11561 (1922); Gummi.Zt. *36*, 869 (1922); C.A. *16*, 1681 (1922). Can. P. 207,717 (1921); R. Age *11*, 12 (1922); See Schidrowitz (36). E.P. 173,546 (1922); Centr. 1922, II, 884; I.R.J. *63*, 293 (1922); Caout. *19*, 11527 (1922); I.R.W. *66*, 549 (1922); Kunst. *13*, 9 (1923); J.S.C.I. *41*, 149a (1922); C.A. *16*, 1682 (1922); Chem. Tech. Übers. *46*, 236 (1922). F.P. 533,198 (1921); Kunst. *12*, 149 & 154 (1922); Chim. & Ind. *8*, 629 (1922). Austrl. P. 16,702 (1920); Chim. & Ind. *7*, 338 (1922).

**Beiersdorf, P.**

1. Solubility of rubber in ether. Pharm. Zt. (1886) p. 187; Centr. (1886) p. 656.

**Bell, P. C.**

1. Contributions to the chemistry of india rubber. I. Action of color, benzene and fatty substances. Gummi. Zt. *8*, No. 10, p. 3 (1894).
2. Same title. II. Action of vegetable and mineral oils. Gummi. Zt. *8*, No. 17, p. 2 (1894).
3. Same title. III. Mineral substances. I.R.W. *10*, 11 (1894); Gummi. Zt. *8*, No. 10, p. 3; No. 19, p. 1 (1894).
4. Same title. IV & V. The action of sulfides of the heavy metals on rubber.

- I.R.W. 10, 58 & 113 (1894); Gummi. Zt. 8, No. 20, p. 1; No. 23, p. 5 (1894).
- Why rubber tires deteriorate. I.R.W. 11, 161 (1895).
  - Cause of decomposition of india rubber proofed goods. I. The effect of dyes and mordants on india rubber. I.R.W. 9, 106 & 182 (1894).
- Ballerio, L.**
- Coagulation with and without acids. See Manders, A. S. (2) p. 49.
- Bencke, A.**
- New work on vulcanization accelerators. Review of Scott & Bedford (1). Gummi. Zt. 35, 898 & 1205 (1921); C.A. 15, 3227 (1921); Centr. 1922, II, 92; Chem. Tech. Ubers. 46, 290 (1922).
  - New investigations on accelerators. Review of Kratz, Flower & Shapiro (1) & (2). R. Age 10, 132 (1921); Gummi. Zt. 35, 1206 (1921); Centr. 1921, IV, 1106.
- Benjamin, E.**
- Prevention of the oxidation of rubber. F.P. 415,177 (1910); J.S.C.I. 29, 1322 (1910).
- Benzinger.** See Anon (241).
- Berghaus, H.**
- Balata. Gummi. Zt. 7, No. 22, p. 2 (1893); Dampf. 9, 855 (1892).
- Bernard, B. H. I.**
- Gutta percha. Agri. Bull. F.M.S. 5, 25 (1916); C.A. 11, 3466 (1917).
- Berniard, R.**
- Dry distillation of rubber. J. Arts & Sciences 21, 19 (1781); Observations and memoirs on physics. Vol. 17, Pt. I, p. 265 (1781); See Tassilly (1) p. 305.
  - Solutions of india rubber applied to the industry. J. Phys. 17, 279 (1784).
- Bernstein, G.**
- Vulcanizing rubber by ultraviolet light. D.R.P. 262,708 (1912); I.R.J. 48, 164 (1914); Centr. 1913, II, 635; Gummi. Zt. 27, 1677 & 1819 (1913); Chem. Ind. 36, 505 (1913); Angew. 26, II, 521 (1913); Caout. 10, 7416 (1913); 11, 7973 (1914); C.A. 7, 3674 (1913); J.S.C.I. 32, 919 (1913); Chem. Tech. Repert. 37, 452 (1913); 38, 222 (1914); Jahresb. Chem. Tech. 59, II, 575 (1913); See Gottlob (6) p. 105; Pearson (1) p. 62; Luckiesch (1) p. 237. E.P. 17,195 (1913); J.S.C.I. 33, 876 (1914); C.A. 9, 395 (1915); I.R.J. 48, 522 (1914); Caout. 13, 9064 (1916); See Luckiesch (1) p. 237. U.S.P. 1,240,116 (1917); C.A. 11, 3470 (1917); I.R.W. 57, 85 (1917); J.S.C.I. 36, 1105 (1917).
  - Studies on the vulcanization of rubber. I. Contribution to the study of the cold vulcanization of rubber. Dissertation. Univ. Clermont-Ferrand. 1912; Kolloid Z. 11, 185 (1912); J.S.C.I. 31, 1087 (1912); Centr. 1913, I, 668 & 2190; Gummi. Zt. 26, 1800 (1912); 27, 470 (1912); 27, 1425 & 1567 (1913); I.R.J. 43, 1359 (1912); C.A. 6, 2546 (1912); 7, 276 (1913); J.C.S. 102, i, 1006 (1912); Genusssm. 32, 543 (1916); Chem. Tech. Repert. 37, 10 (1913); Caout. 9, 6625 (1912); Jahresb. Chem. Tech. 58, II, 597 (1912); Angew. 26, II, 108 (1913); Kunst. 2, 287 (1912); See Porritt (1) p. 52; Gottlob (6) p. 105; (11) part 2, p. 86; Ditmar (49) p. 67.
  - Studies on the vulcanization of rubber. II. Kolloid Z. 12, 193 & 273 (1913); Centr. 1913, I, 2190; 1913, II, 1261; J.S.C.I. 32, 615 (1913); C.A. 7, 3548 (1913); I.R.J. 45, 1296 (1913); J. C. S. 104, i, 638 & 746 (1913); Jahresb. Chem. Tech. 59, II, 580 (1913); Genusssm. 32, 545 (1916); 33, 330 (1917); Chem. Tech. Repert. 37, 401 (1913); J. Frank Inst. 176, 345 (1913); Gummi. Zt. 27, 1425 (1913).
  - Isolation of the insoluble constituent of rubber. Kolloid Z. 15, 49 (1914); Angew. 28, Rep. 24 (1915); J.S.C.I. 34, 500 (1915); J.C.S. 106, i, 1080 (1914); Genusssm. 38, 322 (1919); C.A. 9, 1134 (1915).

5. Vulcanization. See Heilbronner & Bernstein.  
See Torrey & Manders (2) p. 164; C.A. 9, 2005 (1915).
  6. Prevention of black color in litharge mixings.  
F.P. 536,733 (1921); Kunst. 12, 165 (1922); I.R.J. 64, 261 (1922); Gummi. Zt. 37, 177 (1922); Centr. 1922, IV, 1175; Chim. & Ind. Nov. (1922).
- Berry, W. O.**
1. Identification of gutta percha and allied gums by means of their resins.  
J.S.C.I. 23, 529 (1904); Gummi. Zt. 18, 813 (1904); I.R.J. 27, 603 (1904); I.R.W. 30, 297 (1904).
- Berry, A. E. & Boake, A.**
1. Treatment (coagulation) of latex.  
E.P. 16,728 (1913) Roberts & Co. Ltd; J.S.C.I. 33, 758 (1914); C.A. 9, 395 (1915).
- Berthelot.**
1. Universal method for reduction and saturation with hydrogen of organic compounds.  
Bull. soc. chim. 11, (2) 4, 33 & 98 (1869); Ann. Chim. 58, 445; Jahresber. (1869) p. 334; See Harries, Ann. 383, 227; Dubosc & Luttringer (1) p. 172; Hinrichsen & Memmler (1) p. 51; Seeligman, Torrilhon & Falconnet (1) p. 366.
- Bertrand, G.**
1. The tackiness of rubber.  
Caout. 4, 201 (1907); 5, 1440 & 1941 (1908); 6, 3216 (1909); I.R.J. 35, 620 (1908); Gummi. Zt. 22, 1018 (1908); C.A. 2, 2456 (1908); 4, 520 (1910); See Zimmerman (1) p. 253; Hinrichsen & Memmler (1) p. 41 & 46; Gottlob (6) p. 51; Bertrand (2) p. 200.
  2. On the cause of tackiness in india rubber.  
See Spence, D. (8) p. 200.
- Berzelius, J. J.**
1. "Lehrbuch der Chemie."  
Trans. from Swedish by F. Wöhler. Vol. 3, 2 Abt., p. 641. Arnold. 1828.
- Beyer, O.**
1. Preservation of rubber goods.  
E.P. 8,876 (1912); C.A. 7, 3424 (1913); Caout. 11, 7973 (1914); J.S.C.I. 32, 36 (1913).  
F.P. 441,568 (1912); J.S.C.I. 31, 889 (1912).  
F.P. 442,331 (1912); J.S.C.I. 31, 889 (1912).  
D.R.P. 243,248 (1911); J.S.C.I. 31, 291 (1912); Jahresb. Chem. Tech. 58, II, 590 (1912).
- Biddle, A.**
1. Use of casein in rubber.  
U.S.P. 1,437,487 (1922); J.S.C.I. 42, 107a (1923); Caout. 20, 11850 (1923); C.A. 17, 902 (1923).
- Bierer, J. H.**
1. Crimson antimony. Its use in rubber compounding and method of manufacture.  
Chem. Age 6, 194 (1920).
- Biffen, R. H.**
1. Methods of preparing india rubber.  
Bot. Jahresber. 2, 165 (1898); Rev. Chim. Ind. 10, 329 (1899); J. Roy. Soc. Arts 47, 111 (1898); J.S.C.I. 18, 54 (1899); Ann. Botany 12, 166 (1898); Circ. & Agr. J. Roy. Bot. Gardens No. 140, p. 177 (1898); See Wiesner (1) p. 374.
  2. The functions of latex.  
Annals of Botany 11, 334 (1897).
- Bilbrough, C. F. S.**
1. Treatment of latex.  
E.P. 171,046 (1920); Kunst. 13, 9 (1923).
- Bing, K.**
1. Spontaneous changes in vulcanized rubber.  
Kolloid. Z. 4, 232 (1909); 5, 260 (1910); Chem. Tech. Repert. 33, 459 (1919); Jahresb. Chem. Tech. 55, 11,548 (1909) Jahresber. (1909) p. 1042 & 1045; Angew. 22, 2155 (1909); C.A. 3, 1817 (1909); J.S.C.I. 28, 534 (1909); Gummi. Zt. 23, 1047; 24, 356 (1909); Centr. 1909, II, 1090; I.R.J. 37, 685 (1909); See Schidrowitz (6) p. 215; Hinrichsen & Memmler (1) p. 84; Ditmar (49) p. 48; Porritt (1) p. 12.
- Birchall, F. W.**
1. Chloride of sulfur as a vulcanizing agent.

- I.R.W. 15, 90 (1897); Gummi.Zt. 11, No. 23, p. 1; No. 24, p. 2 (1897).
2. Deterioration of india rubber and its cause.  
I.R.W. 13, 39 (1895); Gummi.Zt. 10, No. 16, p. 1 (1896); Wieck's Gewerbezeit. 61, 86 (301).
- Bishop, R. O.**
1. "Undercured" smoked sheet.  
Agr. Bull. F.M.S. 9, 79 (1921); Caout. 19, 11489 (1922); I.R.W. 66, 679 (1922); 67, 94 (1922); C.A. 16, 1884 (1922).
- leBlanc, M. & Kroger, M.**
1. Vulcanization in solution with and without accelerators.  
Zeit. Elektrochem. 27, 335 (1921); I.R.J. 62, 725 (1921); I.R.W. 65, 196 (1921); R. Age 10, 247 (1922); C.A. 16, 174 (1922); J.S.C.I. 40, 667a (1921); Caout. 19, 11284 (1922); Kunst. 11, 173 (1922); Chim. & Ind. 7, 338 (1922); Centr. 1921, IV, 1274; Gummi.Zt. 36, 275 & 531 (1921).
- Bleekrode, S.**
1. Gutta percha of Surinam.  
Amsterdam (1857); See Obach (1) p. 51; Weisner (1) p. 395; Highton, E. (1).
- Bloch, I.**
1. Vulcanization with hydrogen persulfide.  
D.R.P. 219,525 (1908); Centr. 1910, I, 979; C.A. 4, 2211 (1910); Gummi.Zt. 24, 990 (1910); Angew. 23, 1087 (1910); Jahresber. (1910) p. 1122; J.S.C.I. 29, 503 (1910); Kolloid Z. 6, 281 (1910); 7, 160 (1911); Chem. Tech. Report. 34, 172, 451 & 847 (1910); Jahresb. Chem. Tech. 56, II, 580 (1910); Chem. Ind. 33, 189 (1910); See Ber. 41, 1961-85.
- Bloom, D.**
1. Does the acidity of crude rubber resins indicate their botanical origin?  
Science 35, 435 (1912); Angew. 25, 1405 (1912).
- Blossom, T. M.**
1. Physical and chemical properties of rubber and gutta percha.  
Chandler's Am. Chem. 2, 81, 137, 173, 225, 287, 329 & 373 (1871); Mon. sci. 13, 812, 816, 887 & 893 ((1871); 14, 85, 232, 327 & 521 (1872); Jahresber. (1871) p. 811; See Seeligman, Torrilhon & Falconnet (1) p. 356.
- Bobet, R.**
1. Vulcanization problems.  
Caout. 1, 125 (1904); Chem. Tech. Report. 28, 261 (1904).
- Bobilioff, W., Sr.**
1. The reaction of latex of Hevea Brasiliensis.  
Arch. Rubberecultuur 3, 408 (1919); Gummi.Zt. 34, 498 (1920); Chem. Tech. Übers. 45, 8 (1921); C.A. 14, 367 (1920); See deVries (24) p. 25.
- Bobilioff, W., Jr.**
1. Investigation on the formation of latex in Hevea Brasiliensis.  
Arch. Rubberecultuur 3, 374 & 405 (1919); C.A. 14, 1064 (1920); I.R.J. 57, 120 (1919).
- Boehringer, C. H. & Sons.**
1. Process of coagulation of rubber latex.  
F.P. 464,192 (1913); J.S.C.I. 33, 431 (1914).  
D.R.P. 275,716 (1912); C.A. 9, 396 (1913); Chem. Tech. Report. 38, 439 (1914).
  2. Process of preparing rubber mixings.  
D.R.P. 262,563 (1912); J.S.C.I. 32, 919 (1913); Chem. Ind. 36, 505 (1913).
- Boggs, C. R.**
1. Vulcanization with selenium.  
U.S.P. 1,249,272 (1917) Simplex Wire & Cable Co.; C.A. 12, 440 (1918); J.S.C.I. 37, 66a (1918); I.R.W. 57, 288 (1918).
  2. Vulcanization of rubber by selenium.  
J.I.E.C. 10, 117 (1918); C.A. 12, 638 (1918); Angew. 31, II, 446 (1918); Centr. 1919, II, 430; I.R.J. 55, 246 (1918); Gummi.Zt. 34, 576 (1920); I.R.W. 58, 598 (1918); J.S.C.I. 37, 188a (1918); Kolloid Z. 27, 316 (1920); Caout. 15, 9652 (1918); 16, 9693 (1919); 17, 10253 (1920); Chem. News 117, 199 (1918); Chim. & Ind. 1, 311 (1918).

3. Vulcanization accelerators.  
U.S.P. 1,296,469 (1919) Simplex Wire & Cable Co.; C.A. **13**, 1548 (1919); Kunst. **10**, 126 (1920); J.S.C.I. **33**, 379a (1919); Caout. **17**, 10258 (1920).
4. Vulcanizing rubber with selenium and organic accelerators.  
U.S.P. 1,364,055 (1920) Add. to 1,-249,272; C.A. **15**, 776 (1921); J.S.-C.I. **40**, 123a (1921); Centr. 1921, II, 665; Kunst. **12**, 31 (1922); Chem. Tech. Übers. **45**, 128 (1921); Mon. sci. **12**, (5) 5 Brevets; I.R.W. **63**, 339 (1921); See Hemming (1) p. 160.
- Boiry, F.**  
1. Vulcanization of rubber in solution.  
C. r. **175**, 102 (1922); J.S.C.I. **41**, 640a (1922); I.R.J. **64**, 476 (1922); **65**, 433 (1923); J.C.S. **122**, i, 848 (1922); R. Age **12**, 90 (1922); **13**, 154 (1923); I.R.W. **67**, 232 & 361 (1923); Bull. Soc. Chim. Oct. (1922); Chim. & Ind. Nov. (1922); Centr. 1922, IV, 1199; Caout. **19**, 11665 (1922); C.A. **16**, 3772 (1922).
- Bois, E. du**  
1. The preparation of Hevea rubber. (Lecture.)  
Pub. N. I. Landbouw Syndicate 3d year, (1911), Aff. 16, p. 496.  
2. De defaectatie van Hevea-latex.  
Teysmannia **23**, 237 (1912).  
3. Once again on rubber.  
Pub. N. I. Landbouw Syndicate 4th year, (1912), Aff. 1, p. 37.
- Bolas, Thomas.**  
1. The india rubber and gutta percha industries. "Cantor lectures." Lecture I.  
J. Soc. Arts **28**, 753 (1880).  
2. Same title. Lecture II.  
J. Soc. Arts **28**, 763 (1880).  
3. Same title. Lecture III.  
J. Soc. Arts **28**, 773 (1880).  
4. Same title. Lecture IV.  
J. Soc. Arts **28**, 783 (1880).  
5. Same title. Lecture V.  
J. Soc. Arts **28**, 793 (1880).  
6. Same title. Lecture VI.  
J. Soc. Arts **28**, 803 (1880).  
1-6. See R. Age (London) **3**, 542 (1923); I.R.J. **7**, 133 & 149 (1890).
7. Useful and interesting on rubber.  
Gummi. Zt. **5**, No. 9, p. 2 (1891).
8. Vulcanizing gutta percha.  
I.R.J. **1**, 274 (1885).
- Bolton, W. Von**  
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3. Analysis of vulcanized rubber.

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  24. The hydrohalides of natural and synthetic rubber.  
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  25. Contribution to the knowledge of the constitution of caoutchouc and allied compounds.  
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  26. Concerning diacetylpropene (1-5-heptadiene) from rubber.  
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  27. Further remarks on the work of G. Steimmig. "Contribution to the knowledge of synthetic rubber from isoprene."  
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  - Spots on sheets in connection with the use of sulfite and bisulfite.  
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  - The influence on latex of the water used for dilution and its bearing on early coagulation during dilution.  
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**Hayward, N.** (See Anon (63) and (179))

1. Use of sulfur with rubber.  
U.S.P. 1,090 (1839); J. Frank. Inst. 25, 115 (1840); See Meyer, L. O. P. (8); Heinzerling (1) p. 2 & 61; Goodyear, Chas. (4) p. 73, 113 & 164.

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1. On the true value of gutta percha supplied by the "Mimusops" and the "Payena" family of the Sapotaceae.  
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**Hell, A. & Esch, W.**

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C. r. 158, 1343 (1914); J.S.C.I. 33, 653 (1914); I.R.J. 47, 1037 (1914); C.A. 8, 2815 (1914); J.C.S. 106, i, 705 (1914); Centr. 1914, II, 326; Bull. Soc. Chim. 17, (4) 44 (1915); Mon. sci. 81, (5) 463 (1914); Chem. Zt. 38, 1049 (1914); Jahrb. Chem. 24, 416 (1914); See Pearson (1) p. 61.

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See Torrey & Manders (2) p. 156; J.S.C.I. *34*, 562 (1915); C.A. *9*, 2005 (1915); Gummi. Zt. *28*, 1661 (1914); I.R.J. *48*, 164 (1914).

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1. Mechanism of coagulation of certain rubber producing latices.

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1. On the preparation and properties of pure rubber.

Bull. de l'Office Colonial No. 86, 8, 101 (1915); Bull. Agr. Intelligence *6*, 874 (1915); Chem. Trade J. *57*, 360 (1915); C.A. *10*, 399 (1916); Gummi. Zt. *30*, 265 (1915); Chem. Tech. Repert. *40*, 232 (1916); J.S.C.I. *34*, 1062 (1915); Ann. Pl. Ind. Ch. (1915) p. 103.

#### Heineman, A.

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U.S.P. 1,035,788 (1912).

Aust. P. 83,052 (1921); Centr. 1921, IV, 134.

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I.R.W. *67*, 137 (1922).

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I.R.W. *66*, 795 (1922).

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Gummi. Zt. *6*, No. 19, p. 1; *7*, No. 6, p. 1 (1892); *7*, No. 7, p. 3 (1893); Bayer Ind. Gewerbeblatt *24*, 449 (1892); Centr. 1892, II, 762.

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2. The influence of various solvents on the viscosity of rubber solutions.

Comm. Netherlands Gov't. Delft. (1916) p. 470.

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#### Hemming, E.

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Chemical Catalog Co. New York. 1923.



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Caout. 3, 510 (1906); Chem. Tech. Report. 30, 439 (1906); Gummi. Zt. 20, 1227 (1906); J.S.C.I. 25, 940 (1906); I.R.J. 33, 643 (1907); See Ditmar (47) p. 29; Tassilly (1) p. 16; de Vries (24) p. 145; Zsigmondy & Spear (1) p. 254.
2. Coagulation of rubber latex and the elastic properties of pure rubber.  
C. r. 144, 431 (1907); Repert. Gen. Chim. 7, 259 (1907); C.A. 1, 1327 (1907); J.S.C.I. 26, 2641 (1907); Chem. Zt. 31, 331 (1907); I.R.J. 33, 349 (1907); Soc. franc. de phys. No. 257 (1907) p. 2.
3. Physico-chemical studies on rubber. Research on the structure of crude rubber.  
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4. Cinematographic study of the brownian movement of globules in Hevea latex.  
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## 5. Action of ultraviolet rays on rubber.

- Caout. 7, 4371 (1910); Repert. Gen. Chim. 11, 64 (1911); C.A. 5, 1524 (1911); J.S.C.I. 29, 1169 (1910); Gummi. Zt. 25, 118 (1910); Chem. Tech. Report. 34, 563 (1910); See Fonrobert & Harries (1) p. 64; Schidrowitz (6) p. 220; Zimmerman (1) p. 248 & 250; Gottlob (11) part 2, p. 88.
6. Resistance to rupture of rubber obtained by coagulation of latex.  
Caout. 17, 10196 (1920); J.S.C.I. 39, 273a (1920); C.A. 14, 1619 (1920).
  7. Studies on the latex of rubber producing plants.  
See Spence (17) p. 203.

**Henriques, R.**

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2. Contribution to the knowledge of rubber substitutes.  
Gummi. Zt. 7, p. 1 in each of Nos. 17, 18 & 19 (1893); Chem. Zt. 17, 634 & 707 (1893); Mon. sci. 7, 698 & 706 (1893); Ber. 26, 539R (1893); See Schidrowitz (6) p. 173; Ditmar (47) p. 62; (49) p. 67; Hinrichsen & Memmler (1) p. 54; Seeligman, Torrilhon & Falconnet (1) p. 235.
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4. Contribution to the chemistry of india rubber.  
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26. Vulcanization of rubber by rubber halides.  
U.S.P. 1,242,586 (1917) Div. of 112, 187 (1916); C.A. 12, 239 (1918); J.S.C.I. 36, 1243 (1917); Kunst. 8, 144 (1918); Caout. 16, 9691 (1919); I.R.W. 59, 85 (1917).  
Can. Pat. 179,356 (1917) Canadian Consolidated R. Co.; C.A. 12, 324 (1918); I.R.W. 57, 349 (1918).  
E.P. 108,453 (1916); Kunst. 12, 29 (1922); 13, 7 (1923); N. Erfind. Erfahr. 48, 29 (1921); C.A. 11, 3130 (1917).
27. Vulcanization by benzoyl peroxide without sulfur.  
U.S.P. 1,249,181 (1917) Division of 112, 187 (1916) New York Belting & Packing Co.; J.S.C.I. 37, 66a (1918); C.A. 12, 440 (1918); I.R.W. 57, 288 (1918).
28. Organic dyes and low temperature vulcanization.  
Can. Pat. 179,353 (1917); C.A. 12, 324 (1918); I.R.W. 57, 288 (1918).
29. Vulcanization without sulfur.  
Caout. 14, 9119 (1917).
30. Vulcanization by the combined action of sulfur and nitro compounds.  
U.S.P. 1,342,458 (1920) Division of 112, 187 (1916) N. Y. Belting & Packing Co.; J.S.C.I. 39, 552a (1920); C.A. 14, 2430 (1920); I.R.W. 62, 732 (1920).  
Can. Pat. 179,355 (1917) Can. Consolidated R. Co.; C.A. 12, 324 (1918); I.R.W. 57, 349 (1918).
31. Vulcanization at low temperature with benzoyl peroxide, trinitrobenzene or with sulfur and accelerators.  
U.S.P. 1,342,457 (1920) N.Y. Belting & Packing Co.; J.S.C.I. 39, 552a (1920); C.A. 14, 2430 (1920); I.R.W. 62, 732 (1920).  
Can. Pat. 179,354 (1918) Can. Consolidated R. Co.; I.R.W. 57, 349 (1918); C.A. 12, 342 (1918).
32. Vulcanization of rubber.  
U.S.P. 1,433,093 (1922); I.R.W. 67, 153 (1922); J.S.C.I. 41, 989a (1922); C.A. 17, 1352 (1923).
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1. Two new constants of caoutchouc, the elasticity point and the dead temperature.  
Russ. 47, 1401 (1915); J.C.S. 110, i, 55 (1916); J.S.C.I. 35, 58 (1916); Caout. 13, 8864 (1916); C.A. 10, 3176 (1916); Centr. 1916, I, 702; Genussm. 38, 324 (1919); Jahrb. Chem. 26, 175 (1916).
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1. History of the so-called elastifiers and similar additions to rubber.  
Gummi. Zt. 34, 130 (1919); C.A. 14, 367 (1920); Centr. 1920, II, 137; Kolloid. Z. 27, 316 (1920); Jahresber. (1910) p. 1125; See Fonrobert & Harries (1) p. 141; Wo & Wa Ostwald (1).
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1. Contribution to the colloid chemistry of rubber. I. Theory of vulcanization.  
Kolloid. Z. 6, 136 (1910); C.A. 4, 1688 (1910); Mon. sci. 74, (5) 45 (1911); Chem. Tech. Report 34, 280 (1910); Angew. 23, 1086 (1910); J.C.S. 98, ii, 272 (1910); Centr. 1910, I, 2091; II, 927 & 697; J.S.C.I. 29, 890 (1910); Jahresber. (1910) p. 1121; Gummi. Zt. 24, 1172 & 1211 (1910); See Torrey & Manders (1) p. 310; Ditmar (49) p. 67; Gottlob (6) p. 100 & 102; (10) part 2, p. 24; Hinrichsen & Memmler (1) p. 70; Schidrowitz (6) p. 179; Porritt (1), p. 54.
2. Contribution to the colloidal chemistry of rubber. II. Further researches on the theory of vulcanization.

- Kolloid. Z. 7, 45 (1910); J.S.C.I. 29, 891 (1910); Gummi. Zt. 24, 1598 (1910); C.A. 5, 3170 (1911); Chem. Tech. Repert. 36, 656 (1912); See Ditmar (49) p. 67; Porritt (1) p. 59; Gottlob (6) p. 108.
3. Remarks on previous work. See Spence & Young (1).  
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4. Swelling of caoutchouc in various liquids.  
Kolloid. Z. 29, 100 (1921); J.C.S. 120, 1, 733 (1921); Caout. 18, 11104 (1921); I.R.J. 62, 725 (1921); J.S.C.I. 40, 667a (1921); I.R.W. 66, 549 (1922); C.A. 16, 174 (1922).
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D. R. P. 243,346 (1909) Add. to 221,310; Chem. Tech. Repert. 36, 130 (1912); Jahresb. Chem. Tech. 58, II, 590 (1912); Gummi. Zt. 25, 1981 (1911); 26, 783 (1912); C.A. 6, 2333 (1912); See Hemming (1) p. 159.  
E.P. 10,361 (1910); J.S.C.I. 30, 699 (1911); Caout. 9, 6067 (1912).
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E.P. 24,156 (1912); I.R.J. 44, 988 (1912); 46, 260 (1913).

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  2. Studies on vulcanized rubber. On sulfuration of caoutchouc and on some properties of sulfur. C.r. 34, 453 (1852); Inst. (1852) p. 97; J. Pharm. Chim. 21, (2) 366 (1852); Dingl. Poly. J. 124, 131 (1852); Prakt. Chem. 56, 196 (1852); Pharm. Centr. (1852) p. 321; Chem. Gaz. 10, 193 (1852); Jahresber. (1852) p. 637; The Chemist 3, (2) 409 (1851-2); J. Pharm. Sci. 21, (3) 366 (1852); Bull. Soc. d'Encouragement 51, 771 (1852); Am. J. Pharm. 24, (1) 355; See Dittmar (47) p. 62; Heinzerling (1) p. 78; Dubosc (6).



3. On the porosity of caoutchouc relative to the dialysis of gases.

Am. J. Pharm. *39*, (1) 186; Cr. *63*, 533 (1866); Centr. 1867, I, 93; Pharm. Sci. *4*, (4) 357 (1866); Anal. Chem. *6*, 109.

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J. S. C. I. *31*, 1103 (1912); *32*, 179 (1913); C.A. *7*, 905 & 985 (1913); J.C.S. *104*, i, 190 (1913); I.R.J. *45*, 361 (1913); Bull. Imp. Inst. *11*, 162 (1913); Gummi. Zt. *27*, 1220 (1913); Centr. 1913, I, 926 & 1603; Genussm. *28*, 52 (1914); Chem. Tech. Repert. *37*, 158 & 401 (1913); Mon. sci. *80*, (5) 118 (1914); Discussion by Wo. Ostwald; J.S.C.I. *33*, 179 (1913); See Brooks (1) p. 136; Porritt (1) p. 12; Gottlob (6) p. 11; (11) part 2, p. 28.

2. Condensation products of aldehydes and amines as accelerators.

E.P. 7,370 (1914); J.S.C.I. *34*, 436 (1915); *36*, 424 (1917); C.A. *9*, 2468 (1915); J.C.S. *112*, i, 406 (1917); I.R.W. *52*, 595 (1915); Kunst. *11*, 159 (1921); See Stevens (10).

3. Paranitroso-diphenylamine and paranitroso-dimethylaniline as accelerators.

E.P. 10,833 (1914) Add. to 4,263 (1914); J.S.C.I. *34*, 436 (1915); C.A. *9*, 2824 (1914); I.R.J. *49*, 606 (1915); I.R.W. *53*, 12 (1915); Kunst. *11*, 159 (1921); *12*, 148 (1922).

4. Paranitroso-dimethylaniline or its homologues as accelerators.

E.P. 4,263 (1914); I.R.W. *52*, 595 (1915); J.S.C.I. *34*, 368 (1915); Chem. Tech. Übers. *39*, 331 (1915); Kunst. *11*, 95 (1921); C.A. *9*, 2163 (1915).

F.P. 477,586 (1915); J.S.C.I. *35*, 610 (1916); Kunst. *12*, 127 (1922); D.R.P. 323,088 (1915); Kunst. *10*, 222 (1920); I.R.W. *53*, 115 (1915); Centr. 1920, IV, 412; Jahresb. Chem. Tech. *66*, II, 388 (1920); Chem. Tech. Übers. *45*, 128 (1921).

D.R.P. 328,611 (1917) Add. to 323,088; Chem. Tech. Übers. *46*, 59 (1922); I.R.W. *62*, 656 (1920). U.S.P. 1,157,177 (1915); J.S.C.I. *34*,

1155 (1915); C.A. *9*, 3379 (1915); Kunst. *9*, 144 (1922).

Aust. Pat. 82,807 (1915); Kunst. *12*, 28 (1922); Centr. 1921, IV, 271.

Holl. Pat. 2,829 (1919); C.A. *13*, 1408 (1919); I.R.W. *60*, 633 (1919). Can. Pat. 168,806 (1915); I.R.W. *54*, 658 (1916).

5. Nitroso phenols, cresols, etc., as accelerators.

E.P. 101,819 (1916); Kunst. *12*, 7 (1922); J.S.C.I. *35*, 1226 (1916); I.R.J. *52*, 789 (1916); I.R.W. *55*, 266 (1917); C.A. *11*, 308 (1917). F.P. 490,897 (1914); J.S.C.I. *34*, 368 (1915).

D.R.P. 328,611 (1920) Add. to 323,088; Gummi. Zt. *35*, 225 (1920); Kunst. *11*, 15 (1921); Centr. 1921, II, 365; Chem. Tech. Übers. *46*, 59 (1922); Jahresb. Chem. Tech. *66*, II, 389 (1920); I.R.W. *63*, 173 (1920); Zeit. Elektrochem. *27*, 39 (1921).

6. Chlorinated rubber.

E.P. 1,894 (1915); Kunst. *12*, 6 (1922); C.A. *10*, 1950 (1916); I.R.W. *54*, 658 (1916); J.S.C.I. *35*, 479 (1916).

F.P. 480,904 (1916); C.A. *11*, 1338 (1917); J.S.C.I. *36*, 39 (1917).

U.S.P. 1,234,382 (1917); C.A. *11*, 2626 (1917); J.S.C.I. *36*, 1019 (1917).

E.P. 121,091 (1917); C.A. *13*, 676 (1919); Chim. & Ind. *4*, 662 (1920); I.R.W. *59*, 306 (1919).

Can. Pat. 168,807 (1915).

D.R.P. 329,293 (1916); Kolloid. Z. *29*, 150 (1921); Centr. 1921, II, 365; Jahresb. Chem. Tech. *66*, II, 383 (1920); I.R.W. *63*, 173 (1920); Zeit. Elektrochem. *27*, 40 (1921); Chem. Tech. Übers. *46*, 59 (1922); See Lambie (1).

7. Vulcanization accelerators.

I.R.J. *52*, 603 (1916); C.A. *11*, 306 (1917).

8. Vulcanization catalysts.

J.S.C.I. *36*, 950 (1917); C.A. *11*, 3467 (1917); I.R.J. *54*, 407 (1917); Angew. *31*, II, 355 (1918); Caout. *14*, 9363 (1917); *15*, 9638 (1918); Centr. 1918, I, 1214; 1920, II, 136; Kolloid. Z. *27*, 316 (1920).

9. Sulfur reaction products of paranitroso-dimethylaniline as accelerators.

- E.P. 113,570 (1917); C.A. 12, 1352 (1918); J.S.C.I. 37, 216a (1918); I.R.J. 55, 376 (1918); Kunst. 12, 30 (1922); Caout. 16, 9716 (1919); 17, 10157 & 10288 (1920); Chim. & Ind. 1, 429 (1918); Chem. Zt. 46, 240 (1922); I.R.W. 58, 538 (1918).  
D.R.P. 351,974 (1918); Caout. 19, 11560 (1922); R. Age 12, 214 (1922); Kunst. 16, 176 (1922); Gummi. Zt. 36, 954 (1922); Centr. 1922, IV, 255. F.P. 490,965 (1919); Mon. sci. 11, (5) 213 Brevets (1921); Chim. & Ind. 4, 662 (1920); I.R.W. 61, 87 (1919).  
Aust. Appl. Gummi. Zt. 67, 89 (1922).  
U.S.P. 1,443,381 (1923).
10. Organic vulcanization accelerators.  
J.S.C.I. 36, 321 (1917); C.A. 11, 2057 (1917); I.R.J. 53, 291 (1917); I.R.W. 56, 580 (1917).
11. Catalytic acceleration of the vulcanization process.  
J.S.C.I. 36, 424 (1917); J.C.S. 112, i, 406 (1917); I.R.J. 53, 689 & 713 (1917); C.A. 11, 2161 (1919); Kunst. 8, 53 (1918); Gummi. Zt. 32, 477 (1917); Angew. 31, II, 355 (1918); Centr. 1917, II, 839; Bull. Imp. Inst. 15, 450 (1917); I.R.W. 56, 580 (1917).
12. "Accelerene" a catalyst in vulcanization.  
Caout. 15, 9464 (1918); 16, 9784 (1919); C.A. 13, 675 (1919).
13. Action of sulphuryl chloride on rubber.  
E.P. 121,194 (1918); Chim. & Ind. 4, 662 (1920).
14. Vulcanizing rubber with hydrogen sulfide and sulfur dioxide.  
E.P. 129,826 (1919); C.A. 13, 3040 (1919); J.S.C.I. 38, 688a (1919); Caout. 17, 10259 (1920); R. Age (London) 1, 51 (1920); Chem. Met. Eng. 23, 652 (1920); Kunst. 10, 135 (1920); 13, 7 (1923); Gummi. Zt. 34, 78 (1919); I.R.W. 61, 86 (1919).  
D.R.P. 343,181 (1920); J.S.C.I. 38, 688a (1919); Chim. & Ind. 4, 93 (1920); Kunst. 12, 176 (1922); Centr. 1922, II, 94; Gummi. Zt. 36, 317 (1921); I.R.W. 65, 196 (1921); Chem. Tech. Übers. 47, 156 (1923).  
Can. Pat. 215,172 (1922); C.A. 16, 1164 (1922); I.R.W. 65, 422 (1922).  
New Zealand Pat. 44,002; I.R.W. 65, 120 (1921); Kunst. 13, 45 (1923).  
Swiss Pat. 90,484 (1921); Centr. 1922, II, 396.  
Aust. Pat. 88,546 (1920); Kunst. 12, 7 (1922); 13, 45 (1923); Gummi. Zt. 36, 293 (1921).
15. Nitroso benzene as an accelerator.  
E.P. 136,716 (1919); C.A. 14, 1236 (1920); Kunst. 12, 7 & 148 (1922); Caout. 18, 10750 & 10759 (1921); J.S.C.I. 39, 165a (1920); I.R.W. 62, 429 (1920).
16. Vulcanization of cements by sulfur and nitroso benzene.  
E.P. 146,734 (1919); R. Age 7, 510 (1920); J.S.C.I. 39, 605a (1920); I.R.W. 63, 173 (1920); C.A. 15, 452 (1921); Caout. 18, 10847 (1921); Chem. Met. Eng. 23, 1180 (1920); Kunst. 12, 30 (1922); I.R.J. 60, 370 (1920).
17. Vulcanization by sulfur dioxide and hydrogen sulfide. A new vulcanization process.  
I.R.J. 59, 1195 (1920); 60, 839 (1920); Chim. & Ind. 4, 662 (1920); Centr. 1921, II, 132; R. Age 7, 286 (1920); 8, 141 (1920); Gummi. Zt. 34, 972 (1920); J.S.C.I. 38, 688a (1919); J.S.C.I. Ann. Repts. 4, 328 (1919); 5, 332 (1920); 6, 361 (1921); I.R.W. 62, 729 (1920); C.A. 14, 2873 (1920); Caout. 17, 10559 (1920); Centr. 1920, IV, 183; 1921, II, 132; Kunst. 10, 220 (1920); 11, 60 (1921); R. Age (London) 1, 196 (1920); See Stevens (35).
18. Possibilities of the Peachey process.  
I.R.W. 62, 787 (1920); Gummi. Zt. 35, 145 (1920).
19. Procedure of vulcanization of rubber and the resultant product.  
F.P. 516,304 (1920); Caout. 18, 11148 (1921); Kunst. 12, 152 (1922).
20. Vulcanization with hydrogen sulfide and sulfur dioxide under pressure.  
E.P. 162,429 (1921); Add. to 129,826; I.R.J. 62, 172 (1921); Centr. 1921, IV, 430; C.A. 15, 3228 (1921); J.S.C.I. 40, 439a (1921); Chem. Tech. Übers. 45, 231 (1921); Kunst. 12, 31 (1922); I.R.W. 64, 819 (1921); 66, 422 (1922).

- E.P. 129,429 (1921); I.R.W. 64, 820 (1921).  
 Norway Pat. 31,969 (1921); Chem. Tech. Übers. 45, 231 (1921).  
 Aust. Pat. 88,547 (1921); Kunst. 12, 7 (1922); 13, 45 (1923).
21. Cold vulcanization of rubber by gases. (Reply to Dubosc.)  
 I.R.J. 61, 163 (1921); Centr. 1921, II, 565; R. Age 8, 482 (1921); Caout. 18, 10830 (1921).
22. Cold vulcanization. (Lecture.)  
 I.R.J. 63, 427 (1921); J.S.C.I. 41, 310a (1922); Caout. 19, 11362 & 11397 (1922); Kunst. 12, 92 (1922); Centr. 1922, II, 996; I.R.W. 66, 677 (1922); R. Age (London) 3, 61 (1922); Gummi. Zt. 36, 967 (1922).
23. Spreading of vulcanized gels on fabric, paper, etc.  
 E.P. 177,566 (1922) Add. to 129,826; Centr. 1922, IV, 322; C.A. 16, 3234 (1922); Kunst. 13, 9 (1923).
24. The poisonous properties of parani-trosodimethylaniline.  
 I.R.J. 63, 970 (1922); Centr. 1922, IV, 502.
25. The use of sulfur dioxide in the Peachey gas vulcanization process.  
 I.R.J. 64, 944 (1922).
26. Acceleration of the vulcanization of rubber by hydrogen sulfide and sulfur dioxide.  
 E.P. 190,051 (1922); J.S.C.I. 42, 107a (1923); I.R.W. 67, 361 (1923); I.R.J. 65, 332 (1923); Gummi. Zt. 37, 529 (1923); Caout. 20, 11849 (1923).
27. New agents for acceleration of vulcanization and method of production.  
 I.R.W. 60, 633 (1919).
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  18. Contribution to the knowledge of rubber solutions.  
*Chem. Zt.* 34, 471 (1910).
  19. Contribution to the chemistry of rubber. III. Theory of vulcanization. II.  
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  21. Contribution to the chemistry of rubber. IV. Influence of low temperature on the velocity of hot vulcanization and after vulcanization.  
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  22. Solubility of sulfur in rubber.  
*Gummi. Zt.* 27, 1646 (1913); *C.A.* 7, 3670 (1913); *C.A.* 8, 261 (1914); *Centr.* 1913, II, 919; *Chem. Tech. Report.* 38, 223 (1914); *Genussm.* 33, 332 (1917).
  23. A few remarks on the theory of vulcanization.  
*Kolloid. Z.* 12, 84 (1913); *I.R.J.* 47, 34 (1914); *J.C.S.* 104, i, 381 (1913); *Angew.* 26, II, 538 (1913); *C.A.* 7, 2316 (1913).
  24. Dyeing rubber and rubber products.  
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  25. The relationship of mechanical to chemical properties of vulcanized rubber.  
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  26. Organic vulcanization accelerators.  
*J.S.C.I.* 36, 118 (1917); *I.R.J.* 53, 17 & 291 (1917); *I.R.W.* 56, 452 (1917); *C.A.* 11, 1572 (1917); *Caout.* 14, 9159 & 9337 (1917); *Angew.* 31, II, 141 (1918).
  27. Devulcanizing rubber.  
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*U.S.P.* 1,235,852 (1917); *J.S.C.I.* 36, 1056 (1917).  
*E.P.* 126,397 (1917); *Kunst.* 12, 30

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  11. Rubber vulcanization tests. See Eaton & Grantham (3).
 

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  12. The coefficient of vulcanization and the state of cure. See Schidrowitz & Goldsbrough (6).
 

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  24. German synthetic rubber.  
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  27. Slab rubber.  
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J.I.E.C. 13, 519 (1921); Centr. 1921, IV, 1276; I.R.W. 64, 818 (1921); R. Age 9, 250 (1921); C.A. 15, 2748 (1921); J.S.C.I. 40, 709a (1921); Chim. & Ind. 7, 118 & 538 (1922); I.R.J. 62, 305 & 734 (1921); Centr. 1922, II, 266; I.R.J. 62, 291 (1921); See Schidrowitz (30).

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J.I.E.C. 13, 1166 (1921); Centr. 1922, II, 1057; See Stevens (51).

3. The action of heat and light on vulcanized rubber.

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1. Amino guanidine carbonate as an accelerator.

E.P. 17,760 (1915).

2. Caustic dissolved in glycerine as an accelerator.

E.P. 110,059 (1916) Dunlop R. Co.; I.R.W. 57, 211 (1918); J.S.C.I. 36, 1185 (1917); I.R.J. 54, 682 (1917); C.A. 12, 440 (1918); Caout. 15, 9433 (1918).

U.S.P. 1,271,810 (1918); I.R.W. 59, 27 (1918); C.A. 12, 1936 (1918); Chim. & Ind. 2, 698 (1919).

Can. Pat. 185,317 (1918); I.R.W. 59, 142 (1919).

Aust. Pat. 134 (1921); Chem. Zt. 46, 393 (1922).

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D.R.P. 340,491 (1920); Caout. 16, 9734 (1919); Kunst. 10, 135 (1920);

Gummi. Zt. 36, 147 (1921); R. Age 10, 207 (1921); I.R.W. 64, 897 (1920); Centr. 1921, IV, 1038;

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(5) 51 Brevets (1921); I.R.W. 61, 361 (1920); Kunst. 12, 133 (1922).

3. C. O. Weber's test for sun cracking of rubber.

I.R.J. 52, 325 (1916); J.S.C.I. 35, 1027 (1916); C.A. 11, 1337 (1917);

I.R.W. 55, 73 (1916).

4. The chemistry of vulcanization.

J.S.C.I. 36, 782 (1917); C.A. 11, 2073 (1917); Chem. Trade J. 61, 72 (1917); Engineering 104, 134 (1917); I.R.W. 56, 741 (1917); 57,

149 (1917); Caout. 15, 9401, 9437, 9484 & 9609 (1918); Centr. 1918, I,

1213; Ind. 137; Angew. 31, II, 292 (1918); Kolloid. Z. 27, 316 (1920);

I.R.J. 54, 127 (1917); See Brooks (1) p. 137.

5. Vulcanization catalysts.

J.S.C.I. 36, 1072 (1917); I.R.W. 56, 580 (1917); C.A. 12, 332 (1912);

Angew. 31, II, 355 (1918); Centr. 1918, I, 1214.

4.

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C.A. 13, 2299 (1919); Kunst. 12, 30 (1922); 10, 134 (1920); J.S.C.I. 38, 429a (1919); I.R.J. 58, 123 (1919); I.R.W. 60, 633 (1919).  
U.S.P. 1,271,810 (1918); C.A. 12, 1936 (1918); J.S.C.I. 37, 596a; I.R.W. 59, 27 (1918).  
U.S.P. 1,413,813 (1922); J.S.C.I. 41, 426a (1922); I.R.W. 66, 614 (1922); R. Age 12, 332 (1923); Centr. 1922, IV, 591; C.A. 16, 2621 (1922).  
Can. Pat. 192,470 (1919); I.R.J. 61, 25 (1919); I.R.W. 61, 25 (1919).  
E.P. 125,695 (1918); Caout. 17, 10258 (1920).  
F.P. 488,036 (1917); Kunst. 12, 127 (1922).  
Jpn. Pat. 34,944 (1919); C.A. 14, 2430 (1920); I.R.W. 63, 173 (1920); R. Age 10, 55 (1921); Caout. 18, 11028 (1921).
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E.P. 124,276 (1918) Dunlop R. Co;  
C.A. 13, 1652 (1919); I.R.J. 57, 368 (1919); Kunst. 12, 30 (1920); J.S.C.I. 38, 330a (1919); Caout. 17, 10145 (1920); Chim. & Ind. 4, 662 (1920); I.R.W. 60, 633 (1919).  
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I.R.J. 62, 577 (1921); Centr. 1921, IV, 1275.
  12. The discontinuity of vulcanization in the presence of organic accelerators.
 

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  13. Comparison of dimethylamine-dimethyldithiocarbamate and diethylamine-diethyldithiocarbamate as accelerators of vulcanization.
 

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  15. Note on the composition of golden antimony sulfide.
 

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Anon. (39) History of accels. (96) Review of accel. patents. (132) Trade names. (138) A new accel.

Bayer & Co. (19) Accels. with a dissociation constant greater than  $1 \times 10^{-8}$ . (37) See Factis.

Ditmar, R. (62) A mixture of accels. often produces results greater than the sum of the effect of each when used alone.

Dubosc, A. (31) Comparison of org. & inorg. accels. (40) Trade names.

Evans, B. B. (1) Accels. reduce the tearability of R.

Geer, W. C. (5) p. 53. First use of org. accels. by A. H. Marks and Geo. Oenslager in 1906.

Harrison, H. A. & Morton, M. M. (1) Control of high powered accelerators. See Dimethylammonium dimethyldithiocarbamate.

Minatoya, S. & Fukuda, S. (1) Accels. used in Japan. Guanylurea.

Morton, M. M. & Harrison, H. A. (1) Same as Harrison & Morton (1).

North, C. O. (3) R. vulc. with org. accels. has low Sc.

Pickles, S. S. (3) Lecture on org. and inorg. accels. (6) Use of accels. in R. mixes.

Picron, L. (1) Review.

Romani, E. (3) Ultra rapid accels. added to a R-S mix after factory processing by the use of a solution in benzene. Conversely the S is withheld from the R-Accel. mix and dusted on after milling, calendering, etc.

Schidrowitz, P. (29) Use of accels. in thick stocks such as solid tires. (34) Practical accel. difficulties. Scorching prevented by double batch method. Variation of accels. (37) "Catechism on Accels." by a R. manufacturer to an accel. manufacturer.

Spence, D. (27) Claims priority on use of accels.

Twiss, D. F. (5) No known nitroso-accel. is equal to the best basic accels.

Whitby, G. S. (8) Comparison of org. and inorg. accels.

Wilhelm, G. (1) & (3) Accel. patents.

**Accelerene.** See Nitrosodimethylaniline.

**Acetaldehyde.** See Aldehyde-Amines.

Byrne, F. A. (1) See Latex-Coagulants-Aldehydes.

Kerbosch, M. (4) Acetaldehyde in Hevea latex.

Livingston, G. B. & Cairney, W. D. (1) See Latex-Coagulants-Aldehydes.

**Acetaldehyde acetphenylene diamine.**

**Acetaldehyde aniline.**

**Acetaldehyde benzidine.**

**Acetaldehyde benzylamine.**

**Acetaldehyde diethylamine.**

**Acetaldehyde diphenylamine.**

**Acetaldehyde hydroxylamine.**

**Acetaldehyde methylamine.**

**Acetaldehyde mono ethylamine.**

**Acetaldehyde mono methylaniline.**

**Acetaldehyde beta naphthylamine.**

**Acetaldehyde m-nitraniline.**

**Acetaldehyde p-nitraniline.**



**Acetaldehyde phenyl hydrazine.**

**Acetaldehyde p-phenylene diamine.**

**Acetaldehyde o-toluidine.**

**Acetaldehyde p-toluidine.**

**Acetaldehyde m-tolulylene diamine.**

**Acetaldehyde triamidotoluol.**

**Acetaldehyde urea.**

Cadwell, S. M. (3) See Aldehyde-Amines.

**Acetic Acid.** See Latex-Coagulants.

Biffen, R. H. (1) Acetic acid found in smoke used to make Brazilian rubber.

Brindejone, G. (1) See Light.

Martin, W. G. (1) Acetic acid added to R. retards cure.

Obach, E. F. A. (1) No appreciable action on gutta percha.

Stevens, H. P. (30) See Sulfuric Acid.

**Acetone Peroxide.**

Anon. (233) Used as a test reagent for the oxidizing tendency of R.

Twiss, D. F. (3) Weber's sun cracking test.

Weber, C. O. (61) p. 230. A test reagent for the oxidizing tendency of R. See also (18).

**Acetonyl-acetone.**

Bayer & Co. (17) & (18) See Ozone.

Harries, C. (29) Formed by ozonizing R.

Steimmig, G. (1) See Laevulinic Aldehyde.

**Acetphenylenediamine.** See Aldehyde-Amines.

**Acetyl Dinitrodihydrocuminic Acid.**

Ditmar, R. (4) See Nitric acid.

**Acetyl Disulfide.**

Cadwell, S. M. (1) See Xanthates.

**Acetylene.**

Anon. (215) Action of the gas on R.

Dubosc, A. (38) See Distillation of Rubber.

**Acidity.**

Beadle, C. & Stevens, H. P. (3) Acidity of raw rubbers.

Rossem, A. van (4) Acidity in raw rubber. (6) See Acids.

**Acids.** See Hydrochloric, Nitric, Sulfuric, etc.

Camille, A. (5) Effect of acids on R.

Deutsche Peerless G. (1) Acidic R. compounding ingredients such as chlorinated hydrocarbons, wood tars, etc., are treated with pyridine, aniline, quinoline or etc. prior to incorporation into R.

Eaton, B. J. (8) Retarding action of acids due to neutralization of bases present in the R.

Heinzerling, C. (1) p. 29. Dil. acids attack crude R. but slightly.

Herbst, E. & Stern, R. (1) Halogen acids on R.

Kratz, G. D., Flower, A. H. and Shapiro, B. J. (1) Hydrohalides of amino accels. cause retardation of cure as compared with the amines alone.

Newbrough, J. B. (2) An acid resin is added to R. in the mfg. of ebonite.

Rossem, A. van (6) Acidic compounds retard vulc. No relation between acidity of R. and rate of cure. See Sulfur-Coefficient of Vulc.

Schidrowitz, P. (6) p. 216. High grade soft rubbers are relatively stable towards dil. acids.

Seeligmann, T., Torrilhon, G. L. & Falconnet, H. (1) p. 132. Dil. acids attack crude R. but slightly.

Terry, H. L. (1) Action of dil. acids on R. See Nitric Acid.

Thomson, W. & Lewis, F. (1) Effect of acids on cold vulc. R.

**Acids, Organic.** See Oleic Acid.

Badische Co. (8) Synthetic rubber treated with organic acids other than ring carbonic acids or derivatives.

Gorter, K. (11) Non-volatile organic acid isolated from serum solids of latex.

Weber, C. O. (35) See Oils.

**Acid proof goods.**

Weber, C. O. (29) Use of paraffine, ceresin and waxes.

**Acrolein.**

**Acrylic Aldehyde.**

Byrne, F. A. (2) See Latex-Coagulants-Aldehydes.

- Cadwell, S. M. (3) See Aldehyde-Amines.
- Plauson, H. & Vielle, J. A. (1) Condensation products of amines and acrolein are strong accels. of vulc. Acrolein methyl amine.
- Ageing.** See Copper, Depolymerization, Laevulinic Acid, Laevulinic Aldehyde, Light, Manganese, Ozone, Tannin, Heat.
- Anon. (18) Testing the durability of R. goods by exposure to  $O_2$  and  $O_3$ . (35) R. tubing preserved under water, lime water, 1% NaOH solution or 10% glycerine. (83) Ageing at 158° F. vs. natural ageing. (120) The proper temp. for R. store rooms. (124) Colored pigments act as weak preservatives. Blue and violet rays are harmful. Red is inactive. (140) Ageing at 158° F. vs. natural ageing. (141) R. ages very slowly at 15-20° C. (156) MnS improves toughness and ageing. (166) Oils, fats and heat cause poor ageing. Glycerine resists ageing. (170) The best preservative for R. is proper vulc. (172) See Manganese Sulfide. (178) Chrom pigments shorten the life of R. (206) R. preserved by ammonium salicylate or by an alcohol solution of Creolin. (208) Vulc. does not change the affinity of R. for  $O_2$ . Dipping in an alkali solution prevents hardening of R. tubing. (211) Storage of R. goods in winter. (214) Prevention of ageing by  $NH_3$ ,  $(NH_4)_2CO_3$ , caustic, paraffine, glycerine, cresols, phenols, sodium soaps, etc. (293) Ageing of R. insulation. (306) Accelerated ageing tests. Description of.
- Badische Co. (9) Naphthols, resorcinol, etc., added to a R. mix before vulc. to prevent deterioration of the vulc. R. on ageing.
- Barclay, A. (1) R. springs on steam hammers, etc., preserved by submersion in water.
- Bayer & Co. (28)  $NH_3$ , methylamine, piperidine or volatile amine in balloon gases prevent deterioration of the envelope. (42) Aniline, dimethylaniline, ammonia, dimethylamine, NaOH, etc., added to synth. R. prior to vulc. The R. keeps well and vulcanizes easily.
- Beadle, C. & Stevens, H. P. (8) Vulcanizates from resin free R. age poorly.
- Beaver, C. J. & Claremont, E. A. (1) Ageing of sheet R. exposed to rays between the red and the violet.
- Birchall, F. W. (2) Causes of decomposition of R. See Kautschukin.
- Breuil, P. (15) Effect of heat and cold on R. goods.
- Bruni, G. (4) Natural and artificial ageing, both produce laevulinic acid, aldehyde, etc. Ageing in  $CO_2$  under light causes oxidation by decomposition of  $CO_2$  into CO and  $O_2$ .
- Burghardt, C. A. (2) Effect of oils on ageing of rubberized fabric. Facts and reclaimed R. should be used with caution. (3) Excess S. is injurious. Boiling alkali leaves a surface which ages rapidly. Light and impure naphtha are harmful. (4) Oxidized R. forms soaps with caustic. Dyes containing Cu are injurious. The  $O_2$  content of vulc. R. is an index of the extent of deterioration. Mentions Thos. Rowlev's patent. Excess of S oxidizes to  $H_2SO_4$ .
- Cadwell, S. M. (3) Accelerators giving vulc. R. which ages well. See "Aldehyde-Amines."
- Clark, L. (1) Immersion in water prevents deterioration of R.
- Cranor, D. F. (1) See Sulfur-Coefficient.
- Dannerth, F. (4) Pitches increase resistance of vulc. R. to steam, oils or ageing. (6) Under and over vulc. and ageing.
- Dyer, J. W. W. (1) Toluene azo-toluene betanaphthol protects airship fabrics from deterioration.
- Eaton, B. J. (9) See Sodium Carbonate. (25) R. stored on estates 6-12 months does not change appreciably. Surface hardening occurs in 2-3 yrs. Contact with grease is detrimental. (29) Wet R. does not deteriorate on storage. Fast curing R. becomes slower and vice versa.
- Eaton, B. J. & Day, F. W. F. (5) Ageing experiments on vulc. R. First increases then decreases in weight.
- Eaton, B. J. & Grantham, J. (6) See Variability.
- Elworthy, H. S. (1) R. stored in an atmosphere free from  $O_2$ .

- Evans, W. W. (1) 1 day accelerated ageing at 160° F. is approximately equivalent to 6 months natural ageing.
- Foden, N. (1) Lime causes R. to age poorly.
- Fourcroy, A. F. & Vanquelin. (1) Liquid products resulting from the ageing of castilloa R.
- Geer, W. C. (4) Symposium on accelerated life tests.
- Geer, W. C. & Evans, W. W. (1) Artificial ageing tests used for determining proper cure. The R. does not harden but becomes weaker.
- Gottlob, K. O. (7) Over vulc. R. deteriorates more rapidly when an accel. is used.
- Heinzerling, C. (3) R. goods containing mineral pigments age more rapidly than without them. Paraffine and factis retard ageing but make R. more susceptible to heat. The action of alkalis is negligible. Organic fillers make R. less affected by heat. Vulc. R. becomes brittle at 120° C. and may be softened by paraffine although this does not restore elasticity.
- Henriques, R. (4) Vulc. R. heated at 100-120° C. changes and oxidizes. Changes also occur when heated in absence of air. Extracted R. oxidizes more rapidly and free S. exerts a preserving action. Vulc. R. extracted and heated in CO<sub>2</sub> 4 hrs. at 125° C. showed considerable change. Unvulc. R. can be heated indefinitely at 120° C. in CO<sub>2</sub> without change or increase in weight. Free sulfur is a factor in ageing. (5) Ageing tests at 100-120° C. No increase in weight. The higher the S. the higher the O<sub>2</sub> absorbed.
- Hornung, E. & Hansel, S. (1) A mixture of gelatine and oil added to R. prior to vulc. to prevent hardening of the vulc. product.
- Kempel, A. D. (1) Addition of glue to R. improves ageing.
- King, A. H. (3) Literature review on ageing of R.
- Kreussler, U. & Budde, E. (1) Preservation of R. goods by impregnation with paraffine.
- Lascelles-Scott, W. (8) A reducing or deoxidizing powder is desirable in a R. compound. (18) Cuprammonium compounds preserve R.
- Lewton-Brain, L. (2) R. stored in the tropics. Fast curing R. became slower curing and slow curing R. became faster. Slab R. showed no change.
- Lobry de Bruyn, C. A. (1) R. heated in an oven 2 hrs. at 135° C. or in water 4 hrs. at 170° C. should not lose its quality. (2) Sulfur heated 2 hrs. at 135° C. lost only 0.6%. High free S. should condemn any sample.
- Mackintosh, J. G. & Boggett, J. W. (1) See Stearic Acid.
- Marckwald, E. & Frank, F. (10) Artificial ageing in sunlight at 50-70° C. The use of O<sub>2</sub> is impractical. Liquid air used for cold tests. Ultra violet light may be used.
- Martin, R. B. (1) Prevention of oxidation of the surface of vulc. R. goods by painting with a cottonseed oil or glycerine solution of aniline, ethylaniline, dimethyl- $\alpha$ -naphthylamine, oxy-benzoic acid, amido phenol, p-amidobenzyl-dimethylamine or etc. (2) Hardened R. articles are softened with a solution of aniline in cottonseed oil.
- Meyer, L. O. P. (4) Free S. acts harmfully on R. (14) See Gutta Percha.
- Ostromuiskenskii, I. (21) See Piperidine-pentamethylene-dithiocarbamate and Naphthylamines. Aniline retards the ageing of vulc. R. (25) Aniline retards ageing in R. cured without S. by nitro compounds, etc.
- Pellizzola, C. (2) Ageing of R. Review.
- Perrott, G. St. J. & Plumb, A. E. (1) Ageing tests on rubber gas mask fabrics. No relation between natural ageing and tests at 130° C. 15 hrs. exposure to phosgene rots rubber and fabric. 20% carbon black preserves R. in sunlight and weather.
- Riess, P. (1) Surface changes of gutta percha and effect on electrical properties.
- Ruby, I. R. & Depew, H. A. (1) Comparative ageing tests on ZnO and gas black in vulc. R.
- Schidrowitz, P. (44) Discussion of hardening of R. goods and the ageing of R.
- Schidrowitz, P. & Burnand, J. R. (1) Ageing tests on piperidine pentamethylene dithiocarbamate.

- Schulze, E. (3) Factis is not detrimental to a R. mix if properly vulcanized. Warming tests are excellent for determining the ageing properties of R. goods. Bloom preserves R. (6) The oil in cotton deteriorates R.
- Sherman, I. A. (1) Paraffine deteriorates unvulc. R. Proper vulc. insures good ageing.
- Skellon, H. (1) Ageing of vulc. R. free from resins.
- Spiller, J. (1) Effect of light and  $O_2$  on R. "Spiller's resin."
- Springer, G. (1) See Magnesium Carbonate.
- Stevens, H. P. (5) Removal of R. resins causes poor ageing. (6) The stability of vulc. R. and the optimum cure. (18) When Sc is over 3 it tends to increase on ageing. (32) Sulfur-coefficient. (34) Preservation of vulc. R. (45) Ageing of films produced from vulc. R. solutions. Ageing causes further vulc. (49) Samples of plantation R. 3 to 13 yrs. old gave satisfactory vulc. tests. See also (18) & (59). (52) Raw R. ages better than vulc. R. (53) Ageing in dry vs. moist air. Faster in absence of  $H_2O$ . (73). (75) See Sodium Silicofluoride. (78) See Variability. (79) See Sodium Silicofluoride.
- Terry, H. L. (8) Storage of R. goods. Freezing does no harm.
- Thal, J. R. (2) R. goods preserved with  $(NH_4)_2CO_3$ .
- Tollens. (1) Hardening of R.
- Vernet, G. (2) Action of heat, light and moisture on R.
- deVries, O. (24) p. 93. Anti-oxidants.  $NaHSO_3$ ,  $Na_2SO_3$ , etc.
- deVries, O. & Hellendorn, H. J. (6) Excess rolling of wet coagulum, coag. by  $H_2SO_4$  or 100% excess acetic, spontaneous coag., coag. by NaCl or by evaporation, have no effect on the ageing of the vulc. R. (27) Variation in plantation R. diminishes on storage.
- Weber, C. O. (52) Metals which react with  $O_2$  influence the oxidation of R. (61) p. 283. Under vulc. R. more liable to poor ageing than over vulcanized, especially with oils or factis.
- Whitby, G. S. & Walker, O. J. (1) Ageing tests on thiocarbanilide, hexa. and piperidine-pentamethylene-dithiocarbamate.
- Wiegand, W. B. (3) Criticism of Ruby & Depew (1).
- Woodward, van L. (1) See Antimony Sulfides.
- Ageing-Oxidation.** See Copper, Ozone.
- Adriani, A. (1) First analysis of an oxidation product of R. containing 11.4% O. (3) Gutta percha is easily oxidized. One sample contained 20%  $O_2$ .
- Ahrens, F. (1) Light causes oxidation and oxidation causes tackiness. See Viscosity. (2) Theory of the development of tackiness by the action of  $O_2$  and acids. (3) Action of petroleum, benzol, aniline, etc., to restore hardened R. Lasts only as long as the solvent is present. R. should be stored in the dark. (5) The use of vaseline or ceresin for coating R. goods is not practical. (7) Washing and sheeting cause oxidation of R.
- Alexander, P. (2) Sample of Pontianic R. 3 years old had no  $O_2$  content.
- Anon. (32) Literature review. (34)  $K_2CO_3$  or lime in castor oil by aid of heat, used to preserve R. (36) Absorption of  $O_2$  by R. is autocatalytic and accelerated by Mn & Cu. (41) Preservation of R. goods by applying a mixture of gelatine, glycerine & blanc fixe. (82) See Uranium Borate. (135) Retardation of oxidation. (159) See Manganese Sulfide. (205) Quality of R. increases during storage. (214) Preservation of R. by  $NH_3$ ,  $NH_4OH$ , paraffine, alkalies, phenols or petroleum vapors. (233) Test for resistance to oxidation by immersion in a solution of acetone peroxide. (253) Storage of R. goods. Effect of light, moisture and bloom. (277) R. goods should not come in contact with fats or essential oils. (280) R. preserved in 1%  $HCHO$ , 1%  $ZnCl_2$  or in concentrated solution of boric acid. (281) Preservation of R. by  $NH_3$  or glycerine. (283) Hardened R. articles softened in 5% caustic at  $40^\circ C$ . (285) See Copper. (286) Ceresin for preserving R. (287) Effect on tensile of the preservation of R. goods in solutions of lime, alkali, glycerine, ammonia, etc.
- Arens, P. (1) Oxidation during coag. of latex.

- Arppe. (1) Gutta percha is a mixture of the oxidation products of  $C_{10}H_{16}$ .
- Asano, K. (1) Effect of oxidation on viscosity. Products of oxidation of R. are insoluble in benzene.  $CO_2$ ,  $H_2$ , N,  $O_2$  & Air are inactive below  $70^\circ C$ . in absence of light. Cu, light &  $O_2$  cause tackiness. Tackiness lowers the quality of R.
- Badische Co. (1) Bisulfites, thio-sulfates, aldehyde-sulfoxalates or keto-sulfoxalates added to R. before or after vulc. to prevent oxidation. (9) Naphthol, resorcin or quinone in synth. R. before vulc. as age resisters. (10) Aromatic nitro compounds prevent the oxidation of R. (11) Aromatic hydroxy and nitro compounds which retard oxidation added to synth. R. prior to the polymerization process.
- Balland. (1) Changes of vulc. R.  $H_2SO_4$  is removed by dipping in weak alkali solutions or by washing in water.
- Barr, G. (1) Deterioration of balloon fabrics by  $H_2SO_4$ . Lead chromate as a light filter may weaken the fabric. Yellow dyes are not permanent.
- Beadle, C. & Stevens, H. P. (16) Treatment of coagulum with alkali gives a R. which perishes rapidly.
- Benjamin, E. (1) Aniline, alkaloids, dimethyl aniline, etc., dissolved in benzene and painted on rubber articles to prevent oxidation.
- Berry, A. E. & Boake, A. (1) See Latex-Coagulants-Sulfur dioxide.
- Bertrand, G. (1) & (2) Deterioration of R. due to oxidation and not to microorganisms.
- Beyer, C. (1) Preservation of R. by treatment with aqueous emulsions of terpeneol, gum tragacanth, glycerine or aniline.
- Bing, K. (1) Hardening of R. is accompanied by the formation of  $H_2SO_4$ .
- Bolas, T. (2) Heat and fat hasten the oxidation of R. Excess of fat excludes  $O_2$  and retards oxidation.
- Boswell, M. C. (1) Oxidation of R. by  $KMnO_4$ ,  $H_2O_2$ ,  $O_2$  and  $H_2O$ , with iodine.
- Bouffort, M. M. J. (1) An emulsion of bird lime in  $CCl_4$  strengthens perished R.
- Bradley, W. P. (1) Rubber thread protected from oxidation by use of lamp-black and ceresin.
- Breuil, P. (5) See Aluminum Lanolate.
- Burghardt, C. A. (1) Action of air on R. Excess S. in vulc. R. is harmful. Oxidized R. is insoluble in alkalis, benzol, alcohol and ether.
- Camille, A. (6) Ageing and oxidation of R. (7) Excess of S. oxidized to  $H_2SO_4$ . (9) Effect of heat on R. (10) Oils such as palm or cottonseed cause rapid deterioration and oxidation of R. (13) Acetic ether deoxidizes perished R. and removes odor. (19) See Ammonia.
- Caspari, W. A. (1) Gutta percha readily absorbs  $O_2$  and may be preserved in  $H_2$ .
- Chertoff, G. J. (1) Palm, rosin and pine oils or turpentine prevent deterioration of R.
- Chute, H. O. (2) Raw R. preserved with wood tars, pyroligneous acid, etc.
- Coester. (1) Preservation of R. by phenol.
- Danilewski, A. J. (1) Preservation of R. by dilute phenol or glycerine solutions.
- Davidson, S. C. (1) Preservation of R. by  $SO_2$ . See Latex-Preservatives.
- Davis, F. (1) Theory of perishing of R.
- Day. (1) Reduction of oxidation by use of  $NaHSO_3$  in latex.
- Dekker, P. (1) The oxidation products of R. are saponifiable.
- Ditmar, R. (3)  $H_2O_2$  test for oxidizing tendency of R. (18) Effect of resins on oxidation. See Resins. (20)  $ZnO$  increases oxidation of R. in tests at  $100^\circ C$ . for two and one half days. (25) Testing the durability of R. and R. articles by change in weight on heating in oxygen at  $100^\circ C$ . (28) Apparatus for artificial ageing tests on R. (32) Vulc. at low temp. gives better resistance to ageing than at higher temp. (33) Oxidation of reclaimed R. (34)  $BaSO_4$  increases the oxidation of R. when used in large amounts. (46) Ageing is a purely colloidal phenomenon. (47) p. 43. Review of oxidation of R. Chromic acid, K. persulfate and peroxide change R. to an alcohol soluble product. (62) See Manganese Oxide. (63) Basic compounds (aniline) disperse

- colloidal sulfur in R. and increase the life of the R. by keeping the colloid in its disperse phase.
- Ditmar, R. & Dinglinger, O. (1) Factis protects from oxidation. (2) Powdered glass retards oxidation of R.
- Droste. (1) Storage of R. goods.
- Dubosc, A. (15) Use of phenols in coagulation hastens oxidation of the R. (35) See Copper. (36)  $\text{KMnO}_4$ , Br and light on R. (63) Lime and  $\text{MgO}$  cause R. to age poorly. Org. accels. prevent deterioration.
- Eaton, B. J. (9) See Alkali.
- Eichelbaum, G. (1) Hypo-sulfites, sulfoxalates and their aldehyde or keto derivatives added to latex to prevent oxidation.
- Ephriam, J. (1) See Naphthol.
- Estruck, E. de L. (1) Preservation of R. by vaseline and paraffine.
- Fendler, G. & Kuhn, O. (1) R. changes due to other causes as well as oxidation.
- Fonrobert, E. & Harries, C. (1) p. 33. Tannin added during coag. gives a R. more resistant to oxidation.
- General Rubber Co. (7) Latex evaporated in vacuum. The vacuum is released by  $\text{CO}_2$ ,  $\text{NH}_3$ ,  $\text{H}_2$  or  $\text{N}_2$ , giving a R. resistant to oxidation.
- Gorter, K. (10) R. in sealed tubes in  $\text{H}_2$  or  $\text{CO}_2$  does not become tacky. Aldehydes are present in tacky R. Oxidation is not due to enzymes. The oxidation of R. is autocatalytic.
- Granier, E. & Froger-Delapierre, E. L. (1) A mixture of gelatine, albumen, glycerine and triacetin used to protect R. goods from oxidation, oils, grease, etc.
- Grossman, F. (1) Coating R. goods with vaseline or ceresin excludes air and prevents oxidation but the waxes themselves deteriorate R.
- Harries, C. (31) p. 49.
- Heilbronner, A. (1)  $\text{PbO}$  prevents oxidation and resinification in R. cured in hot air. Other mineral and org. reducing agents act the same. Tannin, pyrogallol, p-amidophenol, glycerine, trioxymethylene, hydroquinone and the sulfites of Mg, Ca, Zn or Na. 2-5% Tannin or hydroquinone used in 2 hr. cures at  $130^\circ \text{C}$ .
- Heim, F. & Marquis, R. (1) See Rubber-Purification.
- Hempel, W. (1) Preservation of R. in a chamber over petroleum or in  $\text{CO}_2$ .
- Henri, V. (5) Ultra violet light has no effect on R. in absence of  $\text{O}_2$ . (6) See Latex-Coagulation.
- Henriques, R. (8) Pure R. heated in absence of light absorbs only traces of  $\text{O}_2$ . Vulc. R. under the same condition absorbs  $\text{O}_2$  readily, especially after removal of free S.
- Herbst, E. (1) Passing air thru a benzol solution of R. gave compounds  $\text{C}_{10}\text{H}_{16}\text{O}$  and  $\text{C}_{10}\text{H}_{16}\text{O}_3$ .
- Himmelbauer & Co. (1) Preservation of R. goods by coating with vaseline or ceresin.
- Hinrichsen, F. W. & Marcusson, J. (1) The acetone soluble oxidation products of R. are optically active.
- Hinrichsen, F. W., Marcusson, J. & Quensell, J. H. (1) The oxidation products of R. are optically active.
- Hoffman, A. W. (1) Oxidation of coating on telegraph wires. (2) Gutta is completely changed in air to an alcohol soluble substance.
- Hooper, W. (1) Oxidation destroys the insulating properties of R.
- Hübener, G. (8) On Erdmann's thiozone theory of vulcanization vs. oxidation by air. Ratio of oxidizable S to fixed S in ebonite.
- Hug, E. (1) R. tires, tubes, etc. immersed in an infusion of Roman camomile in castor oil at  $50-80^\circ \text{C}$ .
- Hutchinson, R. (1) Wool cholesterin free from acid prevents oxidation and tackiness.
- Jewett, I. D. (1) Preserving R. by a coating of corn syrup and glycerine.
- Johanson, E. (1) Preservation of R. articles in an atmosphere of  $\text{NH}_3$ .
- Kirchhof, F. (1) Oxidation of vulc. R. for 100 hrs. at  $100^\circ \text{C}$ . changes 10% of the Sc. to  $\text{H}_2\text{SO}_4$ .  $\text{O}_2$  has no effect on viscosity. Rate of oxidation increases with depolymerization. Oxidized R. contains peroxides. (9) Extracted R. oxidizes easily.
- Klaproth, M. H. & Wolff, F. (1) Darkening of R. believed to be due to oxidation. (1807).
- Kuster. (1) Deresinated R. in light and air changes to a brown adhesive mass in one month.
- Larine, J. (1) Phenol, aniline and glycerine used for preserving R. articles.

- Lascelles-Scott, W. (4) Methyl chloride deoxidizes perished R. (5) Petroleum oils shorten the life of R. goods. (6) Turpentine is a powerful oxidizer of R. (11)  $O_3$ ,  $H_2O_2$ ,  $O_2$ , S, halogens, oxidizing agents and acids accelerate the decay of R. Many metals, H,  $CO_2$ , P, reducing agents and weak alkalies retard the decay of R. Any substance lessening the density or increasing the porosity promotes decay. (16) & (17) Deoxidation of old R. by the Cu-Zn couple.
- Last. (1) Oxidation of R. recovered from the nitrosite.
- Leesman, L. & Weinkopf, M. (1) Prevention of suncracking of tires by use of birch tar oil.
- Metzeler & Co. (1) Drying R. in smoke gases to avoid oxidation.
- Mikhaylorskii, I. P. (1) Preservation of R. by covering it with naphthalene powder.
- Miller, W. A. (1) Decay of R. and gutta percha is due to oxidation. Unvulc. Para R. absorbed 2.8%  $O_2$  in 9 months on exposure to light. See Gutta Percha.
- Minder, J. (1) Heat causes tackiness but not oxidation. Light hastens oxidation. The higher the Sc. the slower the oxidation.
- Moore, L. R. (1) Pyrogallol used in R. cements.
- Morgan, S. (1) p. 64. Na bisulfite was introduced by Morgan to prevent surface oxidation.
- Moureaux, C. & Dufraisse, C. (1) Phenolic bodies prevent oxidation of oils, resins, latex and R.
- Muntz, W. E. (1) & (3) Oxidation produces  $H_2SO_3$  and  $H_2SO_4$  in R-S compounds. The action of these acids on the fabric in tires, etc., is prevented by adding basic materials to the R. or fabric before or after vulc.  $Ba(OH)_2$ ,  $(NH_4)_2CO_3$ , lime, etc.
- Obach, E. F. A. (1) Gutta percha should be protected from light and air. See Ozone.
- Ostromuiskii, I. (13) Tannin prevents oxidation of R. 0.5 to 1% of S, nitrobenzene, tannin or amines will not prevent oxidation of R. after it begins. Further heating in vacuum at 120° C. for 3 hrs. stops the oxidation and gives a product which ages well. Synth. and natural R. oxidize rapidly. (11) (19) Vulc. considered as oxidation. Heated R. with 4% of the following at 147° F.  $As_2O_3$ ,  $K_2SO_4$ ,  $CaCl_2$ ,  $K_2Cr_2O_7$ ,  $KClO_4$ ,  $MnO_2$ ,  $K_2Fe(CN)_6$ . Vulc. was not complete.
- Peachey, S. J. (1) R. absorbs 4 atoms of O for each  $C_{10}H_{18}$ . R. resins retard oxidation but do not change the ultimate amount of  $O_2$  absorbed.
- Peachey, S. J. & Leon, M. (1) Oxidation of R. is rapid above 85° C. Natural resins retard oxidation.  $O_2$  on R. forms  $CO_2$ . Action of dry vs. moist  $O_2$  on R. Oxidation of Balata.
- Petsch, T. (1) R. does not become tacky during drying until the moisture is all evaporated.
- Porritt, B. D. (6) Action of  $O_2$  and light on R. Metallic oxides prevent oxidation of R. in dry heat cures.
- Porzel, J. (1) Milling R. in absence of  $O_2$ .
- Pummerer, R. & Burkard, P. H. (1) Oxidation of R. and hydrocaoutchouc. See Hydrogen.
- Pummerer, R. (1) R. in  $C_6H_6$  takes up one half mol.  $O_2$  for each  $C_5H_8$ .
- Ramsay, Chick & Collingridge. (1) Oxygen easily attacks gutta percha. See Albane.
- Revere Rubber Co. (1) Lampblack with ceresin in R. retards deterioration and the action of light.
- Ritter, E. (1) Aniline and hydrazine soften R. and render it easily oxidizable. Preserving R. goods in water the easiest method.
- Rossem, A. van. (2) Oxidation, viscosity and depolymerization. Oxidation is always preceded by depolymerization. (5) Depolymerization and oxidation of raw rubber in air or  $O_2$  at 130° C. No change in vacuo, nitrogen or  $CO_2$ . See Depolymerization.
- Schidrowitz, P. (24) Preservation of R. with glycerine.
- Schulze, E. (3) Air passed into a benzene solution of R. for 24 hrs. at 100° C. ppts. a tarry mass. The evaporation residue is also tarry.
- Schwartz, A. (1) Oxidation of R. in cables caused by oils and reclaimed R. Action of heat on R.
- Simpson, W. (1) R. becomes brittle by action of light. Oxidation products

- are soluble in alcohol and insoluble in benzol.
- Smith, J. (1) Bitumens in R. increase resistance to air, light, acids, alkalis and oils.
- Spiller, J. (1) "Spiller's Resin." First notation of the oxidation of R. to a resinous product.
- Stevens, H. P. (22) Vulc. R. oxidizes more rapidly after alcohol or acetone extraction. Overcured R. with 9% Sc oxidizes more rapidly than with 3% Sc. (34) Preservation of vulc. R. by  $H_2O$  and Kerosene vapors. (43) Storage R. in moist air. (45) Vulc. R. becomes soluble in solvents after long exposure.
- Stowe, F. E. (1) A 10% sol. of  $NH_3$  containing Na oleate, phenolate, etc., applied to the surface of R. goods to prevent oxidation.
- Strunk, H. (1) Oxidation of Funtumia Elastica.
- Swan, J. W. (1) Oxidized R. is soluble in alcohol, insoluble in turpentine and benzol.
- Terry, H. L. (15) p. 73. Review.
- Thal, J. R. (2) R. stored in a chamber over  $(NH_4)_2CO_3$ .
- Thierfelder, R. E. & Schmaelzle, R. (1) Painting tires with a mixture of tar, pitch, resins, etc., to prevent oxidation.
- Thomson, W. (1) Sunlight or boiling water have no action on R. in absence of  $O_2$ . Oils cause rapid oxidation and depolymerization. (3) See Oils.
- deVries, O. (27) Changes in R. on storage. Oxidation lowers tensile and slope.
- Warren de la Rue & Abel. (1) Vulc. R. oxidizes less rapidly than raw R.
- Wattles, J. W. (1) Treatment of R. thread with acetic acid to prevent decay and form a surface glaze.
- Weber, C. O. (1) Cu and Mn pigments cause rapid oxidation of R. (9) See Copper. (28) Increase of acetone soluble in R. by mechanical working is due to depolymerization rather than oxidation. A proper coeff. of vulc. gives good ageing. (31) Albuminous substances in Congo R. cause deterioration. Albumen in R. causes it to become "short" and brittle. (37) Absolutely dry R. oxidizes slowly. (38) Odorless pure R. acquires an odor after oxidation commences. Pigments increase porosity and oxidation in R. (43) Light increases oxidation of R. The lower the degree of vulc. the faster the rate of oxidation. (61) Red lead oxidizes R.
- Weil, R. (1) See Colloid Chemistry of Rubber.
- Whitby, G. S. (1)  $CaCl_2$  increases oxidation of R. (4) Phenols retard oxidation of R. (8) 2 atoms of O combine with each  $C_{10}H_{16}$ . (11) Catalytic oxidation of R.
- Williams, H. J. (2) Oils deteriorate R. Dyes containing Cu are injurious. Oxidized R. is hard and brittle. Free S is injurious.
- Wright, A. W. (1) Ozone on vulc. R. oxidizes S to  $H_2SO_3$  and  $H_2SO_4$ .
- Zimmerman, A. (1) p. 258. Review on oxidation of R.

#### Ageing-Tackiness.

- Accumulatoren-Fabrik Akt. Ges. (1) R. heated in air to fusion, is dissolved in solvents to give a solution of tacky R.
- Anon. (32) Tackiness, bacteria, fermentation, light, heat, acids, etc. Résumé of literature. (248) Thorough drying prevents tackiness.
- Arens, P. (6)  $KMnO_4$  increases tackiness and does not prevent mold.
- Asano, K. (1) Light accelerates tackiness. It polymerizes and depolymerizes R. in an atmosphere of  $CO_2$  where oxidation cannot take place.
- Austriacus. (1) Insufficient drying allows microorganisms to produce tackiness and coloration in R.
- Badische Co. (2) & (3) Heating synth. R. under pressure with nitrogen compounds such as  $NH_3$  to retard the tendency toward tackiness.
- Bamber, M. K. (4) Lecture on the tackiness of R. Not due to bacteria. Creosote prevents tackiness in sunlight.
- Bayer & Co. (1)  $NH_3$ , aliphatic amines or alkalis prevent deterioration of R. (3) Tannin,  $NH_3$ , dimethylamine and dimethylaniline prevent tackiness. (11) Tannic acid as a preservative for synth. R. (16) Tannin prevents oxidation and tackiness of R. (39) Hydroxy- or nitro compounds retard oxidation of R. (41) Aromatic and he-



- terocyclic compounds, or derivatives and substitution products of these compounds, which have two or more amino groups or at least one amino group near hydroxyl groups or substituent groups of the same in the nucleus are added to natural and synth. R. to prevent R., balata or gutta percha from becoming tacky or resinous. Benzyl-m-phenylenediamine, naphthylenediamine, diaminoanthraquinone, benzidine, resorcin,  $\alpha$ -naphthol, dioxnaphthalene, dioxyanthraquinone, aminophenols, aminonaphthols, hydrochinin, pyrogallol, tolidine, diaminocarbazole, diphenyltoluylenediamines, as well as mixtures of these materials are mentioned.
- Bertrand, G. (1) Tackiness in R. is due to an unstable isomer of R. formed by the physico-chemical action of  $O_2$  or light. Not due to bacteria.
- Bing, K. (1) Stickiness of R. due to formation of  $H_2SO_4$ .
- Brindejone, G. (1) There is no increase in weight when R. becomes tacky. R. does not become tacky in absence of light even at high temp. Exposure to light causes tack even when later stored in the dark. See Light.
- Bruni, G. & Pelizzola, C. (1) See Manganese oxide. (2) Tackiness and ageing are chemical processes caused by oxidation.  $O_2$  produces "resins" while  $O_3$  gives laevulinic acid and aldehydes. Cu and Mn aid the oxidation of R.
- Dannerth, F. (6).
- Ditmar, R. (49) p. 48. Tackiness in R.
- Dubosc, A. (64) Alkali or alkaline earth chlorides, NaCl or  $MgCl_2$ , deteriorate R. Moisture aids development of tackiness. When stickiness has begun it cannot be stopped.
- Ephriam, J. (1) Tacky synth. R. improved by partial vulc. with S.
- Fickendey, E. (1) Tackiness is produced by oxidation. Tannin is a preventative.  $H_2O_2$  only affects R. in presence of light. R. reacts with  $O_3$  but  $CO_2$  is not formed. R. in  $H_2$ ,  $N_2$  &  $CO_2$  did not become tacky.
- Frank, F. (4) Wet rubber does not easily become tacky. (8) Deterioration of balloon fabrics by  $H_2SO_4$  and effect of copper. Traces of chlorides, sulfites, etc., in fabric are harmful.
- Flamant, G. (1) See Colloid Chemistry of Rubber.
- Fox, C. P. (1) Effect of Cu on crude R. (2) Tackiness in Guayule R.
- Frank, F. (2) Tackiness is due to insufficient polymerization. (4) Tackiness is produced by any depolymerizing agent, by presence of water or by poor coagulation methods. (5) Tackiness in raw R.
- Frank, F. & Marckwald, E. (2) Absence of light or heat, the presence of moisture and special coag. methods, prevent tackiness. (3) Neither bacteria nor enzymes cause tackiness although they hasten it.
- Gardner, H. C. T. (2) Tackiness prevented by preparing R. pure and free from  $H_2O$ . Tackiness usually due to bacterial action on albuminoids.
- Gorter, K. (6) Autooxidation and tackiness. (7) Light causes tackiness in air and  $O_2$  but not in  $H_2$  or  $CO_2$ . Sample of Hevea R. in sunlight for 4 years was not tacky. Tests on Borneo R. in air,  $O_2$ ,  $H_2$  &  $CO_2$ . The sample in  $O_2$  became liquid. Palm oil is detrimental to R. Non-tacky R. is meta stable. Tacky R. is the stable form. (9) Distillation of tacky R. gives a dilute solution of an aldehyde. (11) Stable and meta stable forms of R.
- Gottlob, K. (1) Both chemical and physical changes cause tackiness. Tacky R. retains its tendency to become tacky after vulc.
- Hinrichsen, F. W. & Memmler, K. (1) See p. 46.
- Hornung, E. & Hansel, S. (1) Vulc. oils or insoluble glue prevent tackiness in R.
- Jacobson, F. (1) Cause of tackiness.
- Kawakami, K. (1) Theories regarding tackiness, depolymerization and chemistry of vulc. of R.
- Kerbosch, M. (1) Summary of literature on tackiness (1913). (3) Summary of literature on tackiness. Evaporated latex becomes less tacky than coagulated R. Quebrachite does not affect oxidation. Egg white prevents oxidation.
- Kogakushi, K. (1) Effect of light, Cu,  $O_3$ ,  $O_2$ , air,  $N_2$ ,  $H_2$ ,  $CO_2$ , etc., on tackiness and depolymerization.

- Polymerized R. is insoluble in benzene. Ageing tests at 70° C.
- Koller, P. (1) See Potassium Sulfide.
- Marquis, R. & Heim, F. (1) Tackiness is caused by oxidation. Smoked R. does not become tacky.
- Marx, T. & Zimmerman, A. (1) Effect of Cu and Fe salts, bacteria, decay of protein or serum, light, heat, coagulants, milling, etc., on tackiness.
- Morgan, S. (1) p. 161. Tackiness caused by Cu, light, O<sub>2</sub> and heat. See Enzymes.
- Ostromuiskii, I. (12) Tackiness is produced by oxidation and facilitated by catalysts.
- Ostwald, Wa. (1) and
- Ostwald, Wo. & Ostwald, Wa. (1) Prevention of hardening or tackiness in raw or vulc. R. by dimethylaniline, pyridine, quinoline, alkaloids or nitrogenous compounds. Added before or after coagulation and before or after vulc.
- Raymond, J. M. (1) Production of tack on the surface of vulc. R. articles by dipping in a hot solution of KMnO<sub>4</sub>.
- Rossem, A. van. (1) Effect of light on viscosity and tackiness.
- Schidrowitz, P. (6) Alkalies promote and acids retard tackiness. Antiseptics do not always prevent tackiness. (17) Tackiness implies depolymerization and may be independent of bacteria.
- Schulze, E. (1) Oxidation causes tackiness. A good R. will not become tacky at 100-110° C. for a short time.
- Scott, J. (1) Tackiness is due to bacteria.
- Spence, D. (15) Enzymes do not cause tackiness. (16) Cause of tackiness in raw R.
- Spence, D. & Russell, W. F. (1) Tacky R. treated with alkali metals, their alloys or with caustic.
- Steinitzer, F. (1) CO<sub>2</sub> causes tackiness. Effect of phenol on R.
- deVries, O. (24) p. 361. Review of tackiness and its causes.
- Weber, C. O. (61) p. 31. Alkalies cause R. to become tacky.
- Weil, R. (1) See Colloid Chemistry of R.
- Whitby, G. S. (1) Describes a sample of R. left in 25% H<sub>2</sub>SO<sub>4</sub> without becoming tacky. Excess of HCl for coagulation causes tackiness, as well as caustic alkalies and Cu. (2) Sunlight first depolymerizes R. Oxidation then follows. (8) p. 104. Aluminum coagulating vessels do not cause tackiness. (10) Resin content increases with tackiness. Tackiness developed by heat is different from that produced by sunlight.
- Zingler, M. (1) & (2) Hardened R. treated with tartar emetic and tannin. Tacky R. treated with CaSO<sub>4</sub> and tannin for 1-2 days.
- Akbar.**
- Horan, C. F. (2) Secret accel. of the Fisk Rubber Co.
- Aksel.**
- Anon. (93) Non toxic hot air accel. Works well with reclaimed R. and can replace PbO.
- Alban.**
- Albane. C<sub>30</sub>H<sub>30</sub>O<sub>2</sub>. m.p. 160° C.
- Allen. (1) p. 158. Abstracts of literature.
- Anon. (196). (219) Albane is not detrimental to gutta percha. Contains 15%.
- Bornträger, H. (1) Albane is a mixture of several resin oils. Albane products and fluavile are oxidation products of gutta percha.
- Ditmar, R. (12) & (45) Sec Gutta Percha. (38) Albane from gutta percha.
- Harries, C. (7) Albane like crystalline solid (C<sub>30</sub>H<sub>30</sub>O<sub>2</sub>)<sub>2</sub>, from Ficus Magnoloides Borci.
- Montpelier, J. A. (1) Separation of albane and fluavile by alcohol.
- Oesterle, O. (1) Analysis of. (2) Albane does not affect the properties of gutta percha.
- Oudemans, A. C. (1) Analysis of.
- Payen, M. (1) Crystalline constituent of gutta percha.
- Ramsay, Chick & Collingridge. (1) Albane, an oxidation product of gutta percha. Properties and analysis.
- Razmann, R. (1) Alban. C<sub>30</sub>H<sub>30</sub>O<sub>2</sub>. m.p. 195° C. Physical and chemical properties given.
- Sahlfield, F. (1) See Gutta Percha.
- Spence, D. (4) Alpha-alban (m.p. 201°

- 205° C.) and beta-alban (m.p. 154° C.) isolated from resin of *Ficus Vogelii*.  $C_{16}H_{32}O$ .
- Tschirch, A. (2) & (4) Albane from gutta percha. (3) Constitution of gutta percha resins.
- Tschirch, A. & Müller, O. (1) Albane from New Guiana gutta percha. (2) from Sumatra gutta percha.
- Albumin.** See Proteins.
- Anon. (84). (250) Albumin, proteins and their Ca or Mg. salts, blood meal, bean meal as accelerators.
- Eaton, B. J. (8) An accel. of vulc.
- Esch, W. (13) Egg albumin added to synthetic R. The dry distillation product of blood albumin replaces R. resins in a PbO-R mix.
- Johnson, J. Y. (1) Synthetic rubber heated with albumin to improve quality.
- King, A. H. (1)
- Lascelles-Scott, W. (1) See Latex.
- Weber, C. O. (31) See Ageing-Oxidation.
- Aldehydes.**
- Gorter, K. (10) See Ageing-Oxidation.
- Aldehyde-Amines.** See Acetaldehyde, Acrylic aldehyde, Benzaldehyde, n-Butyl aldehyde, Cinnamic aldehyde, Citronellal, Dextrose, Formaldehyde, Furfural, Glucose, Heptaldehyde, Methylene Aniline, Methylene diphenyldiamine, Propionaldehyde, Valeraldehyde.
- Bastide, J. (1) Methylene and ethylene compounds of fatty and aromatic amines are sulfur solvents and accels. of vulc.
- Bayer & Co. (19) Condensation products of ammonia and aldehydes as accel. of vulc.
- Cadwell, S. M. (3) Reaction products of an aldehyde having 2 or more carbon atoms in an open chain with an amine. General claim of open chain aldehydes having 2-7 carbon atoms with an amine having a dissociation constant greater than  $1 \times 10^{-12}$ . These organic accels. are slightly accelerated by ZnO. The natural amines in the R. will react with these aldehydes producing new accels. 1% heptaldehyde on 100 pts. R.
- Dubosc, A. (32). (54) Furfural condensation products of ammonia and amines as accels. of vulc.
- Naylor, R. B. (1) Condensation products of formaldehyde and para toluidine as accel. of vulc.
- Peachey, S. J. (2) Condensation products of aldehydes with ammonia or amines as accels. of vulc.
- Ricard, E. (1) Condensation products of furfural with ammonia or amines as accels. of vulc.
- Romani, E. (4) See Vulcanization-Theories.
- Aldehyde Ammonia.** See Vulkacite.
- Bayer & Co. (19) Wholly or partially reacted upon by S, during vulc. See Aldehyde-Amines. (20) Method of manufacture. (24) Used in compounds softened with petrolatum or aniline. See Aniline.
- Bedford, C. W. & Sebrell, L. B. (1) Reacts with S. at 80° C. forming ammonium polysulfide and a reddish brown resin.
- le Blanc, M. & Kroger, M. (1) Effect on viscosity of cements. See Viscosity.
- Ditmar, R. (62).
- Dubosc, A. (17) A powerful org. accel. (30).
- Eaton, B. J. (8).
- Endres, H. A. (1) Comparison of accels.
- Geer, W. C. (2).
- King, A. H. (1).
- Murriel, P. I. (5).
- Peachey, S. J. (2) See Aldehyde-Amines.
- Pearson, H. C. (1) p. 83.
- Pickles, S. S. (4).
- Rosenbaum, J. L. (1) Decomposes on the mill.
- Rossem, A. van (6) Comparison with piperidine and p-nitroso dimethylaniline by means of coef. of vulc.
- Schidrowitz, P. (19). (52) See Latex-Vulcanization.
- Scott, W. & Bedford, C. W. (1) Liberates  $NH_3$  during vulc. forming basic alkylated pyridine derivatives.
- Seidl, E. (4) Tabulation of compound-ing data.
- Shepherd, N. A. & Krall, S. (2) See Hexamethylenetetramine.
- Stevens, H. P. (45) Vulc. of R. in solution.

- Twiss, D. F. (4) R-95, S-5.0, Accel.-1.0. Cured 90 Min./40 lbs. Shows 0.17% free S. as against 3.6% without accel. (12).
- Twiss, D. F. & Brazier, S. A. (1) Effect of increased amount of accel. & temp. on rate of cure.
- Twiss, D. F., Brazier, S. A. & Thomas, F. (1) Does not require inorganic accel. for activation.
- Twiss, D. F. & Howson, C. W. H. (1) ZnO used with aldehyde ammonia speeds first part of cure, lowers maximum tensile and slightly increases the range.
- Twiss, D. F. & Martin, G. (1) Detect this accel. in the fresh vulcanizate by the odor of a freshly cut surface.
- Twiss, D. F. & Thomas, F. (1) Used in differentiating between activity of various forms of S.
- Weber, L. E. (9) More active than hexa, thiocarbonyl or formaldehyde aniline. Causes scorching. Not over 1% should be used.
- Williams, C. S. (1) Tabulated compounding data. Works well in pure gum stock without secondary accels. ZnO has little if any effect. MgO retards.

**Aldehydes and Ammonium Polysulfide.**  
Bruni. (6) See Dithio acids.

**Aldehyde Resin.**

- Ephriam, J. (1) See Naphthol.

**Aldehyde-Sulfoxalates.**

- Badische Co. (1) See Ageing-Oxidation.
- Eichelbaum, G. (2) See Latex-Coagulation and Ageing-Oxidation.

**Alkali.**

- See Ammonia, Potassium hydroxide, Sodium hydroxide, Sodium carbonate.
- Badische Co. (7) Treatment of synth. R. with caustic.
- Bayer & Co. (15) Treatment of synth. R. with caustic.
- Bing, K. (1) Caustic prevents tackiness in vulc. R. by neutralizing  $H_2SO_4$ .
- Cadwell, S. M. (5) See Amines.
- Camille, A. (19) Weak alkali solutions have no effect on R. in the cold. On warming they cause R. to become glutinous.

- Eaton, B. J. (6) See Natural Accelerators. (9) Effect of alkalis on crude R. Poor ageing after vulcanization.
- Eaton, B. J. & Day, F. W. F. (1) Alkali used in the preparation of R. causes an increase in the rate of cure.
- Editorial. (1) Alkalies are deleterious to R.
- Heinzerling, C. (1) p. 29. Conc. alkalies have only a slight effect on crude R.
- Henri, V. (1) Alkalies inhibit coagulation.
- King, A. H. (1) (5).
- Martin, W. G. (1) Effect of the alkali used in reclaiming.
- Meyer, E. E. A. G. (6) Alkalies as accels. "Catalpo R" accelerates vulc.
- Richards, Taylor & Wylde. (1) R. is vulc. by heating in an alkaline solution of S.
- Schidrowitz, P. (6) p. 216. Stability of R. towards alkalies at high temp.
- Schon & Son. (1) See Rubber-Purification.
- Seeligmann, G., Torrilhon, G. L. & Falconnet, H. (1) p. 132. Conc. caustic alkalies only slightly attack crude rubber.
- Spence, D. (29) Alkali salts of aniline and fatty acids as accels. of vulc.
- Stevens, H. P. (71) See Latex-Preservatives.
- Twiss, D. F. (6) Caustic dissolved in aromatic hydroxy compounds as an accel.
- Weber, C. O. (61) p. 31. See Ageing-Tackiness.
- Wilderman, M. (1) Manufacture of ebonite resistant to alkalies.

**Alkali Chlorides.**

- Dubosc, A. (64) See Ageing-Tackiness.

**Alkali Polysulfides.**

**Alkali Sulfides.**

- See Ammonium polysulfide, Ammonium sulfide, Polysulfides, Potassium polysulfide, Potassium sulfide, Sodium polysulfide and Sodium sulfide.

**Alkalized Cresol.**

- Davidson, S. C. See Latex-Preservatives.

**Alkaloids.** See Quinine, Quinidine.

- Benjamin, E. (1) See Ageing-Oxidation.
- Fawcitt, C. A. (4) See Aniline.

Ostwald, Wo. & Ostwald, Wa. (1) See Ageing-Tackiness.

**Alkyl derivatives of Lead and Mercury.**

Marzahn, R. (1) p. 467. Accels. of vulc. of R.

Spence, D. (29) Accel. of vulc.

**Allyl Sulfide.**

Olivier, H. P. M. A. (1) See Light.

**Alum.** See Latex-Coagulants.

Garnier, E. (1) Vulc. of R. with alum without S.

**Aluminium (metal).**

Breuil, P. (5) Al Zn & Ni, used in ebonite to give brilliant color.

Day. (1) Al gives better heat conductivity in thick R. articles.

Seidl, E. (1) Al has higher heat conductivity than PbO but will not vulcanize a R-S mix under the same conditions.

Thomson, W. & Lewis, F. (1) See Copper.

**Aluminium Hydroxide.**

Frood, F. & Alger, H. P. (1) Fireproofing R.

Hartong, R. C. (2) Mixed with R. as a water paste and dried before mixing other ingredients.

Perkin, W. H. & Mandleberg, J. H. (1) R. rendered non-inflammable by incorporating large amounts of Al hydroxide.

**Aluminium Lactate.** See Latex-Coagulants-Aluminium Lactate.

**Aluminium Lanolate.**

Breuil, P. (5) Preserves R. and makes it more pliable.

**Aluminium Oxide.**

Breuil, P. (5) Inert white pigment, resistant to acids and high temperatures.

Eaton, A. K. (2) Used as a compound-ingredient in R.

Gnädinger, J. (1) See Latex.

**Aluminium Sulfite.**

Dieffenbach, G. (1) See Ebonite.

**Amines.**

Cadwell, S. M. (5) & (6) Effect of Amines on the accelerators as listed under Zinc Xanthogenates, Cadwell

(5). One half the mol. wt. of aliphatic amine based on the CS<sub>2</sub> content of the principal accel. gives the greatest activation. Excess of primary aliphatic amines retards the cure. Excess of secondary aliphatic amines is less effective. Excess of tertiary aliphatic amine has no retarding effect. Dibenzylamine, aniline, p-toluidine and sodium hydroxide are specifically mentioned as aids for thiol salts.

Dubosc, A. (17) Discussion of Ostromuiskii, I. (17). Aromatic amines as accels.

Ostromuiskii, I. (17) Amines retard vulc. with S. in absence of metallic oxides. Tertiary amines are inactive. Aromatic amines have little effect. Amines retard vulc. with nitro compounds. Aliphatic amines heated with S remain unchanged, but with metallic oxides and S. at 180° C. they form trithio-ozonides. See Trithio-ozone and Vulcanization-Theories.

**Amino Acids.** See Natural Accelerators.

Johnson, J. Y. (1) Heat synthetic R. with amino acids to improve quality.

**p-Aminoazobenzene.**

Gottlob, K. O. (8) A weak accel. for synth. R.

**p-Aminobenzylaniline.**

Bedford, C. W. & Scott, W. (1) Equal to methylene-diphenyl-diamine in curing power.

**Aminocymene.** (Amino methyl isopropyl benzene.)

Andrews, C. E. (1) More rapid accel. than aniline, wt. for wt. Its hydrochloride may be used.

Dannerth, F. (1)

**p-Aminodimethylaniline.**

Bedford, C. W. & Sebrell, L. B. (1) A R. cement of this material with S and ZnO will air cure on the addition of CS<sub>2</sub>.

Bedford, C. W. & Sibley, R. L. (2) Prepared by H<sub>2</sub>S on p-nitrosodimethylaniline. (3) Reaction product of H<sub>2</sub>S, p-nitrosodimethylaniline and CS<sub>2</sub> as an accel. of vulc.

LeBlanc, M. & Kröger, M. (1) See Viscosity and Colloid Chemistry of Rubber.

- Ditmar, R. (62).  
 Dubosc, A. (40).  
 Eaton, B. J., Grantham, J. & Day, F. W. F. (1) The hydrochloride retards vulc. of a fast curing R.  
 Meeus, E. de. (1) Mentions the hydrochloride as an accel. of vulc.  
 Murrill, P. I. (5).  
 Peachey, S. J. (3) Prepared by reduction of p-nitro dimethylaniline.  
 Spence, D. (28) An accel. and also used for the devulcanization of R.

**Aminoguanidine.**

- Dubosc, A. (40).  
 Twiss, D. F. (4) An unstable accel. best used as its bicarbonate salt. R-95, S-5, Accel.-1, cure 90/40 lbs. Free S-0.89%. Without accel. 3.6%.

**Amino-methyl-isopropylbenzene.** See Aminocymene.

**Aminonaphthol.**

- Bayer & Co. (41) See Ageing-tackiness.  
 Ditmar, R. (58) See Dyes.

**p-Aminophenetol** (p-phenetidine).

- Kratz, G. D., Flower, A. H. & Coolidge, C. (1) Discussion of Spence (29).  
 Spence, D. (29) A powerful catalyst. The ortho isomer is only weakly active. Has better curing power than p-amino phenol.

**m-Aminophenol.**

- Bayer & Co. (41) See Ageing-Tackiness.  
 le Blanc, M. & Kröger, M. (1) An accel. of vulc.

**p-Aminophenol.**

- Bedford, C. W. & Sebrell, L. B. (1) Will vulc. a R. cement in the presence of S, ZnO and CS<sub>2</sub>. See p-p-Dihydroxy-diphenyl-thiourea.  
 Boggs, C. R. (2).  
 Dubosc, A. (40) produces H<sub>2</sub>S by action with S during vulc.  
 Heilbronner, A. (1) See Tannin.  
 Kratz, G. D., Flower, A. H. & Coolidge, C. (1) Has more curing power than aniline.  
 Martin, R. B. (1) See Ageing.  
 Peachey, S. J. (7) Has no appreciable action on vulc.  
 Spence, D. (29) A weak accel. p-Amino phenetole is more active.

- Stevens, H. P. (29) Inactive as an accel. of vulc.

**p-Aminothiobenzanilide.**

- Bedford, C. W. & Scott, W. (1) Formed by action of S on methylenediphenyl-diamine or p-amino-benzylaniline.

**Ammonia.** See Ageing-Oxidation, Ageing-Tackiness, Latex-Preservatives.

- Anon. (261) & (262) NH<sub>3</sub> retards rate of cure of unsmoked sheet when added to latex. Tensile strength and chemical composition remain unchanged.  
 Badische Co. (8) Heating synthetic R. with NH<sub>3</sub> to improve quality.  
 Bayer & Co. (15) Treatment of synthetic R. with ammonia, aniline or dimethylaniline. (42).  
 Bedford, C. W. & Scott, W. (1) NH<sub>3</sub> is liberated during vulc. by the reaction of S on Hexa.  
 Bedford, C. W. & Sebrell, L. B. (1) Aldehyde ammonia reacts with S at 80° C. liberating NH<sub>3</sub>, therefore this reaction takes place during vulc.  
 Blossom, T. M. (1) Ammonia water in contact with R. for some time forms an emulsion. NH<sub>3</sub> gas has no action on R.  
 Boggs, C. R. (3).  
 Bourn, A. O. (2) Vulc. of R. in an atmosphere of NH<sub>3</sub> gives increased tensile strength.  
 Cadwell, S. M. (3) See Aldehyde-Amines.  
 Camille, A. (19) NH<sub>3</sub> or weak alkaline solutions do not harm the quality of R. and even impart a certain degree of "resisting" power. In warm alkaline solutions R. becomes glutinous without dissolving.  
 Campbell, L. E. (4) NH<sub>3</sub> retards rate of cure of unsmoked sheet when added to latex.  
 Cayla, V. (1) Ammonia causes an intense yellow color in the latex of Ficus Vogelii.  
 Ditmar, R. (47) p. 51. Ammonia emulsifies R.  
 Dubosc, A. (41) Devulcanization with NH<sub>3</sub>. See Hexa.  
 Eaton, B. J. (16) Ammonia added during coagulation retards vulc.  
 Edwards, J. D. & Pickering, S. F. (1) Permeability of NH<sub>3</sub> thru R.

- Geoffrey, & Delore, G. (1) Vulc. with the aid of  $\text{NH}_3$  gas under pressure.
- Gorter, K. (11)  $\text{NH}_3$  identified in serum of latex after coagulation with acetic acid.
- Heinzerling, C. (1) p. 29. R. forms an emulsion with ammonia after long digestion.
- deJong, A. W. K. & Tromp de Haas, W. R. (1) Ammonia does not precipitate R. contrary to Meyen (1).
- Koller, P. (1) Ammonia gives an emulsion with R.
- Lucas, W. (1) Coagulation time increased by using  $\text{NH}_3$  but no more acid is required.  $\text{Na}_2\text{CO}_3$  is as efficient as  $\text{NH}_3$ . Ammonia used on trees facilitates flow of latex.
- Marquard, F. (1) R. in  $\text{CHCl}_3$  treated with  $\text{NH}_3$ , after removal of solvent mixed with calcium phosphate to make white ivory like material. R. in  $\text{CHCl}_3$  bleached with chlorine prior to incorporating fillers to make ivory like material. (2) R. in  $\text{CHCl}_3$  treated with  $\text{NH}_3$  to bleach it. Calcium phosphate or zinc carbonate added to make white ivory like products.
- Mathews, R. (1)  $\text{NH}_4\text{OH}$  has no effect on R. (1805).
- Meyen. (1) Ammonia precipitates R. of a greenish color.
- Moureley. (1) Vulc. R. with 2-3% S in 12% ammonia solution or in  $\text{NH}_3$  vapor. (1884).
- Muntz, W. E. (1) Vulc. R. is treated with  $\text{NH}_3$  either before or after formation of acids due to oxidation of S. (3) Oxy-sulfur acids and anhydrides formed during vulc. are neutralized by treating with  $\text{NH}_3$ .
- Obach, E. F. A. (1) Conc.  $\text{NH}_4\text{OH}$  has no action on gutta percha.
- Ose, Y. (1)  $\text{NH}_3$  gas developed from a powder used to expand rubber shoes cured in molds. No mention of curing power.
- Poizot, E. (1) Sponge R. by use of ammonia.
- Rowley, T. (1) R. articles containing S vulc. by  $\text{NH}_3$  gas with heat and pressure or by aqueous solutions.
- Schidrowitz, P. (51) See Latex-Vulcanization.
- Schmidt, E. A. (1) Conc.  $\text{NH}_4\text{OH}$  swells R. and on long standing changes it to a sticky mass.
- Schulze, E. (1) Schulze was never able to dissolve crude R. in  $\text{NH}_4\text{OH}$ .
- Scott, W. & Bedford, C. W. (1) S reacting on p-phenylene diamine liberates  $\text{NH}_3$  during vulc. Diphenylguanidine said to form  $\text{NH}_3$  by reaction with  $\text{H}_2\text{S}$  during cure.
- Sumers. (1) Finely cut R. dissolves in conc.  $\text{NH}_4\text{OH}$  in about four months.
- Tilche, E. (1) Vulc. of R. in an atmosphere of  $\text{NH}_3$  or other volatile alkali.  $\text{H}_2\text{S}$  or  $\text{CO}_2$  may be added.
- Venable, C. S. & Fuwa, T. (1) Solubility in R.
- Weber, C. O. (48) Ammonia causes a slight yellow greenish coloration and coagulation of R.
- Ammonium Borate.**
- Anon. (84).
- Bayer & Co. (19).
- Ditmar, R. (62).
- Eaton, B. J. (8).
- King, A. H. (1).
- de Meeus, E. (1).
- Rossem, A. van. (6) Comparison with other ammonium salts as an accel.
- Ammonium Bromide.**
- Bourn, A. O. (2) See Vulcanization.
- Ammonium Carbonates.** See Latex-Preservatives.
- Bayer & Co. (19).
- Bourn, A. O. (2) See Vulcanization-Methods.
- Dubosc, A. (17) Equal to amino guanidine as an accel. of vulc.
- Griffen, J. T. (1) Henderson used this material in 1887 at Oswego, N. Y., to make sponge R.
- Hancock, C. (2) Making sponge R.
- Rossem, A. van. (6) Comparison with other ammonium salts by their effect on the Coefficient of vulc.
- Schidrowitz, P. & Goldsbrough, H. A. (4) Ammonium carbonate added to latex to produce R. for use in making sponge R.
- Schulze, E. (4) Ammonium carbonate and nitrate used to make R. balls. The ammonia which diffuses thru the R. combines with the free S.
- Twiss, D. F. (4) An effective accel. R-95, S-5, Accel.-1. Cure 90 Min./40 lbs. Free S. 1.39%. Without accel. free S. 3.6%.

**Ammonium Cyanide.**

Dubosc, A. (30) Reacts with S during vulc. to form HSCN and H<sub>2</sub>S.

**Ammonium Dithiocarbamates.**

Cadwell, S. M. (5) (6).  
Maximoff, A. (1).

**Ammonium Iodide.**

Bourn, A. O. (2) See Vulcanization-Methods.

**Ammonium Salts.** Chloride, Nitrate, Oxalate, Phosphate, Sulfate.

van Rossem, A. (6) Comparison by effect on Sc. Phosphate is a weak accel. The oxalate is inactive, the others are retarders.

**Ammonium Sulfide.**

American Chemical Society. (6).  
Bedford, C. W. & Sebrell, L. B. (1)  
Vulc. by NH<sub>4</sub>SH in absence of free S is due to liberation of free S by oxidation. Paraphenylene diamine and aldehyde ammonia react with S during the cure to form ammonium polysulfides.  
Bruni, G. (6) See Dithio acids.  
Kratz, G. D., Flower, A. H. & Shapiro, B. J. (1) Vulc. of R. by NH<sub>4</sub>SH in absence of free S.

**Ammonium Trithiocarbonate.**

Bedford, C. W. & Sebrell, L. B. (1)  
Does not gel a R-S-ZnO cement. (2).

**Ammonium Xanthates.**

Cadwell, S. M. (4) (5) (6). See Xanthates.

**Amyl Acetate.**

Ahrens, F. (1) See Viscosity.

**Amyl alcohol.**

Dubosc, A. (30) & (40) See Peachey Process.  
Twiss, D. F. (6) Caustic alkalies dissolved in this alcohol for use as an accel. of vulc.

**Amylamine.**

Gorter, K. (11) Amylamine is formed by loss of CO<sub>2</sub> from leucine and may therefore be one of the natural accels. in R.  
Morton, H. A. (1) Tertiary amylamine, benzylidene tertiary amylamine, tertiary amylborate, carbonate, stearate

or other derivatives of the amine are used as accels. of vulc.

Ostromuiskii, I. (31) Isoamylamine and PbO used with S for vulc. at low temperatures.

**iso-Amylamine-isoamylidithiocarbamate.**

See Dithiocarbamates.  
Maximoff, A. (1) A strong accel.  
Ostromuiskii, I. (31) Cures R. at ordinary temp. with S and PbO.

**Amylborate.** See Amylamine.

**Amylcarbonate.** See Amylamine.

**Amyl Xanthates.**

Cadwell, S. M. (1) (4) (5) See Xanthates.

**Amyrin.**

Cohen, N. H. (3) See Lupeol. (4)  
Alpha amyrol and beta amyrol, C<sub>30</sub>H<sub>50</sub>O, found in breck.

**Amyrin Acetate, alpha and beta.**

Cohen, N. H. (2) African R. contains beta amyrin acetate. Lupeol was not present in the R. A phytosterol isolated from the resin, identical with iso-cholesterol from wool fat.  
Hillen, G. H. (1) Alpha and beta amyrrin acetate are present in Jelutong or Pontianac R. and Malaluwai gutta percha. See Resins and also Gutta Percha.  
Ultee, A. J. (16) Alpha and beta alban isolated by Spence, D. from R. of Ficus Vogelii are actually alpha amyrrin acetate and lupeol acetate.

**Anhydroformaldehyde aniline.** See Methylene Aniline.

**Anhydroformaldehyde p-phenylene diamine.**

Kratz, G. D., Flower, A. H. & Coolidge, C. (1) Comparison of the mono- and di-anhydro compounds. See Aniline.

**Aniline.**

Anon. (80) Manufacture of. (95) Aniline poisoning and treatment of same. (111) Affects nervous system and destroys red corpuscles. (121) Aniline dissolves 5% S at 130° C.  
Badische Co. (8) Heating synthetic R. with aniline to improve quality.



- Bayer & Co. (15) Used to make synthetic R. and left in to act as an accel. during vulc. (19) Mixtures of aniline with bromides or iodides as accels. (24) Aniline, alkylanilines, xylenes, dimethyl-p-toluidine, petrolatum, linseed oil, castor oil, paraffine, etc., used to increase plasticity of vulc. R. (34) See Antimony Oxides.
- Bedford, C. W. & Sebrell, L. B. (1) & (2) Curing cements at room temperature by aniline and other amines with  $\text{CS}_2$  and  $\text{ZnO}$ .
- Beyer, C. (1) R. articles preserved by treatment with aqueous emulsion of aniline.
- Cadwell, S. M. (1) Aniline activates the disulfides of thiocarbonic acids as well as their metallic salts. See Xanthates. (3) See Aldehyde-Amines. (5) See Amines.
- Davis, P. A. (1) Effect of aniline and homologues on the human system.
- Deutsche Peerless Gesellschaft. (1) R. ingredients which are acidic are treated with pyridine, aniline or quinoline. The products so treated vulc. more rapidly.
- Ditmar, R. (18) Accelerates cure by increasing dispersion of R. colloid and ease of absorption of S.
- Dubosc, A. (17) Aniline was first org. accel. used in U. S. (30) At the vulc. temp. of  $140^\circ \text{C}$ . aniline reacts with S as follows:  $\text{C}_6\text{H}_5\text{NH}_2 + 4\text{S} = \text{HSCN} + 2\text{C}_2\text{H}_2 + \text{H}_2\text{S} + \text{CS}_2$ . (34) As a reclaiming agent, removes only a trace of combined S. (41) Devulcanization with aniline. See Hexa.
- Earle, D. (1) Data on Aniline poisoning. See Poisons.
- Endres, H. A. (1) Comparison with other accels.
- Fawsitt, C. A. (4) First use of aniline and alkaloids in 1890 in vulc. of R. by sulfur and antimony iodide.
- Geer, W. C. (5) p. 53. First used as organic accel. by A. H. Marks and George Oenslager in 1906 at Diamond R. Co.
- Gottlob, K. O. (7) (8) An accel. and preservative in synthetic R.
- Hasselt, J. F. B. van. (1) See p-Nitrosodimethylaniline.
- King, A. H. (1) An accel.
- Kirchhof, F. (3) See Tetrabromide.
- Kratz, G. D., Flower, A. H. & Coolidge, C. (1) Comparison of accels. in R-92.5 and S-7.5. All cures 90 Min./ $148^\circ \text{C}$ . Figures are parts by weight necessary to give same coefficient of vulc.
- |   |       |
|---|-------|
| Aniline .....                             | 1.000 |
| Urea .....                                | 0.250 |
| Thiourea .....                            | 0.300 |
| Monophenyl-thiourea .....                 | 0.450 |
| Monophenyl guanidine .....                | 0.075 |
| Diphenyl guanidine (sym.) ....            | 0.075 |
| Triphenyl guanidine .....                 | 0.500 |
| Anhydro formaldehyde aniline.             | 0.750 |
| p-phenylene diamine .....                 | 0.170 |
| Mono-anhydro-p-phenylene<br>diamine ..... | 0.140 |
| Di-anhydro-p-phenylene<br>diamine .....   | 0.140 |
- Substitution of phenyl group for hydrogen in amino or imino group decreases accel. power. Substitution of second amino group in aniline gives greater increase in curing power than substituting methylene group for amino hydrogen. Curing power of thiocarbanilide and triphenyl guanidine ascribed to liberation of aniline. Mechanism for action of aniline given.
- | Wt. | Accel.                   | S. Coef. |
|-----|--------------------------|----------|
| 0.0 | Control .....            | 1.937    |
| 1.0 | Phenol .....             | 1.779    |
| 1.0 | Hydroquinone .....       | 1.561    |
| 1.0 | p-amino phenol .....     | 5.210    |
| 1.0 | Aniline .....            | 4.614    |
| 1.0 | p-phenylene diamine .... | 7.955    |
- Kratz, G. D., Flower, A. H. & Shapiro, B. J. (1) Aniline more active in pure gum stock than thiocarbanilide. Reverse is true in presence of  $\text{ZnO}$ .  $\text{ZnO}$  retards action of aniline but gives same maximum tensiles as thiocarbanilide. There is no relation between accelerating power and dissociation constant as shown by the activity of the following accels. Aniline, methylaniline, dimethylaniline, p-toluidine, m-phenylene diamine, p-phenylene diamine, Benzidine, phenyl hydrazine, hydrazobenzene. (2) Effect of  $\text{ZnO}$  on aniline and thiocarbanilide. There is no relationship between physical properties and coefficient of vulc. of accelerated mixes.
- Meyer, E. E. A. G. (1) Aniline and petrolatum in R.

- Muntz, W. E. (1) Fabrics treated with aniline to neutralize acids which may form from rubber in contact with it.
- Murrill, P. I. (5) Solvent for R. Acts as softener and prevents scorching on mill as well as being an accel.
- Ostromuilevskii, I. (13) & (17) Aniline and S form trithioaniline which is stable and incapable of functioning as a S carrier. Aromatic amines have low accelerating power.
- Ostwald, W. & Ostwald, W. (1) In 1908 patented use of aniline (3%) to prevent the ageing or hardening of R.
- Pearson, H. C. (1) p. 82. See Poisoning.
- Pickles, S. S. (4).
- Rosenbaum, J. L. (1) Used in U. S. prior to first Bayer patent.
- Schon & Son. (1) See purification of R.
- Scott, W. & Bedford, C. W. (1) Aniline is a "hydrogen polysulphide accel." Mechanism of accel. explained by formation of a derivative of ammonium polysulfide.
- Simmons, H. E. (1).
- Spence, D. (27) Aniline and sodium used for devulcanization. (28) An accel.
- Twiss, D. F. (7) Sodium, potassium or NaOH in aniline as an accel.
- Twiss, D. F. & Brazier, S. A. (1).
- Weber, L. E. (9) Works equally well in presence or absence of ZnO. Gives variation due to losses during mixing. Use decreased due to its toxicity.
- White, N. S. (1) Aniline used in rubberized fabrics in 1884 to give "brilliance of color to pigments."
- Whittelsey, T. T. (1) Aniline used to neutralize acids in vapor cured R.

**Aniline black.**

Anon. (122) Mentioned as an accel.

**Aniline Sulfate.**

Bayer & Co., (32) An accel. when used in small amounts. (34) See Antimony Oxides. (35) Aliphatic or aromatic amino compounds such as diethylaniline used with aniline sulfate and a metallic oxide or peroxide.

**Aniline yellow.** See Auramine O.

**Anthracene.**

Lascelles-Scott, W. (15) A preservative for R.

**Anthraquinone.**

- Anon. (84) An accel.
- Bayer & Co. (35) Used with peroxides which give oxygen at vulc. temp.
- Ditmar, R. (62) 3-5% in a factis mix shortens the cure from 120 min. to 30 min.
- Eaton, B. J. (8).
- King, A. H. (1).
- Pearson, H. C. (1) p. 87.
- Ricard, E. (2).

**Antifebrin.**

Ditmar, R. (62) Shortens the cure but makes the R. porous.

**Antimony.** See Metals.

**Antimony Bromide.** See Antimony Iodide.

**Antimony Dithiocarbamates.**

Molony, S. B. & Nikaido, Y. (1) (2). See Dithiocarbamates.

**Antimony Iodide.** (Bromide Chloride.)

- Fawsitt, C. A. (3) 15% of the iodide and 6% S cures at 200° F. or 10 min./250° F. Tin iodide and bromide mentioned. (4) Mixtures of R., S and other ingredients cured by iodides or bromides of Sb, Sn, Hg, Zn, Pb, or Bi with a metal (Pb), an alkaloid or a base (aniline). Transparent products can be made.
- Frood, F. & Alger, H. P. (1) Fire-proofing R.
- Terry, H. L. (6) Antimony iodide and S form sulfur iodides which vulc. the R. See Sulfur Chloride.
- Thomson, W. (6) R. vulc. with antimony iodide is insol. in C<sub>6</sub>H<sub>6</sub>.
- Weber, C. O. (4) Fawsitt's Sb iodide forms SbSI from which Iodine is liberated.

**Antimony Oxides.**

- Bayer & Co. (33) Antimony pentoxide as an accel. produces a red vulcanizate. (34) & (35) Sb<sub>2</sub>O<sub>3</sub>, PbO, PbO<sub>2</sub>, etc., with amines such as aniline, aniline sulfate or diethylaniline, give greater strength and extensibility.
- Ditmar, R. (22) See Antimony Sulfides.
- Maximoff, A. (1) Almost inert with thiuram mono- and disulfides.
- Pearson, H. C. (1) p. 90. Used in coloring dental vulcanite.

**Antimony Sulfides.** See Polysulfides.

- Alcock, F. H. (1) Variability. Presence of  $\text{CaS}_2\text{O}_3$ .
- Anon. (111) Crimson antimony more soluble in digestive juices, therefore more poisonous than golden antimony. (118) Crimson antimony used as vulc. agent because of free S. Color stable at high temp. (158) Specifications for use. (160) Effect of acid in. (161) Antimony sulfide increases the life of R. (255) Vulc. with Sb sulfides only slightly affected by org. accel. except where S is added as such.
- Bell, P. C. (4) Early use of.
- Bierer, J. H. (1) Crimson antimony in R. compounding.
- Breuil, P. (7) Manufacture and properties of. Black antimony sulfide is not a vulcanizer. (8) Antimony sulfide in presence of lime gives violet coloration and loses its effectiveness.
- Burke, W. H. (1) Vulc. of R. with "Kerme's Mineral" without use of free S.
- Clemens. (1) Free acid in antimony sulfide detrimental to R. (1888).
- Ditmar, R. (18) Preparation and properties of antimony sulfide. It is non-poisonous. (22) Antimony oxides change to sulfides during vulc. (62) No accel. power after removal of free S.
- Dubosc, A. (11)  $\text{Sb}_2\text{S}_3$  decomposes to  $\text{Sb}_2\text{S}_5$  at  $135^\circ \text{C}$ . giving S available for vulc.
- Falke, O. & Richards, A. C. (1)  $\text{Sb}_2\text{S}_3$  and  $\text{Na}_2\text{SO}_3$  for vulc. without S.
- Gerner, H. (2) See Mercuric sulfide.
- van Geuus, Jan.** (1) Use in R. in 1848.
- Gottlob, K. O. (6) p. 69. Non-poisonous.  $\text{Sb}_2\text{S}_3$  has no vulcanizing action.
- Hancock, C. (2) Used to vulc. gutta percha (1847). (4) Used with other metallic sulfides to vulc. gutta percha.
- King, A. H. (1) Antimony sulfides accelerate vulc.
- Kirchhof, F. (8) Chemistry of golden sulfides.
- Klenker. (1) Composition of.
- Lascelles-Scott, W. (1) These sulfides facilitate vulc. (1892). (37).
- Luff, B. D. W. & Porritt, B. D. (1) Availability of S in  $\text{Sb}_2\text{S}_3$  for vulc.
- Mayall, T. J. (1) Vulc. of ebonite by antimony sulfide without free S.
- Ostromuiskii, I. (25) See m-Dinitrobenzene.
- Peachey, S. J. (4) Accels. have little effect when antimony sulfides are used without free S.
- Peachey, S. J. & Skipsey, A. (2) Tends to prevent vulc. of R. by  $\text{H}_2\text{S}$  and  $\text{SO}_2$ .
- Phelps, E. B. & Stevenson, A. F. (1) Use in articles for infants is undesirable.
- Pickles, S. S. (4) Vulc. of R. by  $\text{Sb}_2\text{S}_5$  without free S.
- Rogers, H. (1) First used by C. Hancock in 1846.
- Rossem, A. van & Dekker, P. (2) Analyses.
- Roussel, V. (1) Use in R. industry (1882).
- Schidrowitz, P. (6) p. 190. Improves quality and accelerates vulc.
- Shirk, D. A. (1) Pentasulfide has higher curing power than trisulfide.
- Shirk, D. A. & Wilson, N. R. (1) Composition of commercial grades.
- Short, A. & Sharpe, F. H. (1) Composition and use.
- Tassilly, E. (1) p. 227. Used as coloring and vulcanizing agent.
- Twiss, D. F. (15) Composition of golden antimony.
- Weber, C. O. (61)  $\text{Sb}_2\text{S}_5$  will not vulc. R. without free S.
- Weber, L. E. (9) Hexa and triphenyl guanidine may be used with antimony sulfides.
- Winkler, C. (1) Vulc. of R. with.
- Wleck, W. (1) Composition of.
- Woodward, van L. (1) First used as R. pigment in 1852 by Wm. Forster. Eliminates excess S and prevents blooming. Heat resistance and ageing qualities are increased.

**Antimony Thiolidide.** See Phosphorous Thioiodides.**Antipyrine.**

- Anon. (84) An accel.
- Ditmar, R. (62).
- Ricard, E. (2).

**Arsenic Dithiocarbamates.**

- Molony, S. B. & Nikaido, Y. (1) & (2) See Dithiocarbamates.

**Arsenic Iodide.**

- Thomson, W. & Lewis, F. (1) On cold cured R. a drop of arsenic iodide

liberates iodine. Not true with sulfur cures.

**Arsenic Sulfides.**

- Hancock, C. (2) Vulc. with  $As_2S_3$ .  
 Lascelles-Scott, W. (30) So toxic that it should not be used in R.  
 Marzahn, R. (1) p. 467.  $As_2S_3$  assists vulc.  
 Pearson, H. C. (1) p. 91.  
 Schulze, E. (10) Used to vulc. hard R. and waterproof goods and as a red pigment.

**Arsenic Thiobromide (thioiodide).** See Phosphorous Thioiodides.

**Arsenic Xanthates.**

- Cadwell, S. M. (2) & (5) See Xanthates.

**Arsenic Yellow.**

- Lascelles-Scott, W. (32) Poisonous and therefore has but limited application.

**Artificial Musk (trinitro-butylxylene).**

- Ostromuiskii, I. (25) & (30) Will vulc. R. when used with  $PbO$ . See Nitrobenzene and m-Dinitrobenzene.

**Asphalts.**

- King, A. H. (2) Retarders of vulc.

**Atropine.**

- Blanc, M. le & Kröger, M. (1) See Colloid Chemistry of Rubber.

**Auramine O.** Aniline yellow. Imido-tetramethyl diamido diphenylmethane.

- Gaisman, L. & Rosenbaum, J. L. (1) R.-57,  $ZnO$ -40, S-3, dye base-1.0. Cure 1 hr./40 lbs. Uncured stock deep yellow. Cured stock is white.  
 Mecus, E. de (1) Free dye base is an accel.  
 Rosenbaum, J. L. (1) Requires  $ZnO$  to bring out full curing power.

**Aurantica.** Hexanitrodiphenylamine.

- Ostromuiskii, I. (21) A dye and a vulc. agent (with  $PbO$ ).

**Aureolin Yellow (Potassium cobalto nitrite).**

- Lascelles-Scott, W. (32) & (33) Better covering power than  $CdS$ . Well adapted for use in R.

**Aurotin (Tetranitrophenolphthalein).**

- Ostromuiskii, I. (16). (21) Both a dye and a curing agent with  $PbO$  and without S. Product reddish brown, very resistant to heat and ageing. (22). (25) See Dinitrobenzene. (30).

**Azo-dicarbo-diamidine.**

- Dubose, A. (40) An accel.

**Azotetrazol.**

- Dubose, A. (40) An accel.

**Bacteria.** See Enzymes.

**Balafluavil.**

- Tschirch, A. & Schereschewski, E. (1) See Balata.

**Balalban.**

- Tschirch, A. & Schereschewski, E. (1) See Balata.

**Balata.** (B)

- Anon. (5) Historical summary of B. patents. (260) B. from northern Nigeria.  
 Berghaus, A. (1) Caustic alkalies and conc.  $HCl$  do not attack B. Conc.  $H_2SO_4$  evolves  $SO_2$  and chars it.  $HNO_3$  attacks it and forms hydrocyanic and formic acids.  
 Bleekrode, S. (1) B. introduced into Europe in 1857.  
 Caspari, W. A. (1) Evolution of  $H_2S$  noted during vulc. of Balata and Gutta percha.  
 Cohen, N. H. (1) Crude B. yields a lupeyl ester in addition to beta-amyril-acetate and beta-balalban. See Lupcol. See Phytosterol.  
 Dekker, P. (1) Extraction of B. and gutta percha.  
 Ditmar, R. (22) Chlorine in  $CHCl_3$  solution of B. gives white product of formula  $C_{10}H_{12}Cl_6$ , difficultly soluble in  $C_6H_6$  and unattacked by conc.  $HNO_3$ . Fuming  $HNO_3$  on B. gives a yellow amorphous acidic product. (29) B. vulc. with increasing amounts of S. (38) Albane from B. (40) A new B. resin.  
 Edison, T. A. (1) See Chlorinated rubber.  
 Lenz, W. (1) Analysis and properties of B.

Ostwald, W. & Ostwald, W. (1) Prevention of hardening and oxidation by use of amines, alkaloids, etc.

Spence, D. (25) At an S content of 3%, B. undergoes a sudden change in physical properties in the direction of R. (29) Vulc. of B. with S and a catalyst.

Spence, D. & Kratz, G. D. (1) Insoluble matter of B. a complex of protein and carbohydrate.

Spence, D. & Young, J. (2) Rate of combination with S same as for R.

Sperlich, (1) Analysis of B. B. not as easily altered in air and light as gutta percha.

Tschirch, A. & Schereschewski, E. (1) From alcoholic solution of B. isolated: alpha balalban,  $C_{27}H_{42}O_2$ , m.p.  $230^{\circ}$ - $231^{\circ}$  C.; beta balalban,  $C_{27}H_{40}O_2$ , m.p.  $108^{\circ}$ - $109^{\circ}$  C.; balafluavil,  $C_{27}H_{40}O$ . Esters of cinnamic or other acids not present in B. resins. Some gutta percha samples contain cinnamic acid esters, and others do not.

Wiesner, J. (1) Properties of B. same as in Berghaus, A. (1).

#### **Barium Chloride.**

Breuil, P. (4) Poisonous. Not used in R.

Zimmerman, A. (3) See Latex-Coagulants-Salts.

#### **Barium Hydroxide.**

Dubosc, A. (30) Reacts with S during vulc. to form  $H_2S$  and  $SO_2$ .

Gottlob, K. O. (6) p. 71. No action as an accel. of vulc.

Rossem, A. van. (6) Comparison with other inorganic accels.

#### **Barium Oxide.**

Gottlob, K. O. (7) Inactive in S cures.

Ostromuiskenskii, I. (13) An accel. for S cures. (19) (21) & (25)  $BaO$  activates nitro compounds in vulc. without S.

#### **Barium Peroxide.**

Bernstein, G. (6) See Lead Sulfide.

Dubosc, A. (30) See Peachey Process.

Kratz, G. D., Flower, A. H. & Shapiro, B. J. (1) Mentioned.

Ostromuiskenskii, I. (11) & (15) Will not vulc. R.

#### **Barium Sulfate.**

Breuil, P. (4) No effect on strength and extensibility of R. High  $BaSO_4$  content increases tendency to oxidation of R.

Ditmar, R. (34) High  $BaSO_4$  content increases tendency to oxidation of R.

#### **Barium Sulfide.**

Breuil, P. (4) An agent of vulc. but without any advantages.

Gerard, A. (1) First used by G. to vulc. R. by replacing S.

Heinzerling, C. (1) p. 65. 10-15%  $BaS$  or  $CaS$  in R. gave good cure on heating at  $132^{\circ}$ - $145^{\circ}$  C.

Pearson, H. C. (1) p. 64. Vulc. of R. by.

#### **Barium Thiosulfate.**

Lascelles-Scott, W. (28) A soft white pigment. Non-poisonous. Slowly decomposes in contact with R.

Levinstein, E. (1) Vulc. of R. by. One atom of S from each molecule is available for vulc.

#### **Barium Xanthates.**

Cadwell, S. M. (1) (4) (5) & (6) See Xanthates.

#### **Beet sugar residue.**

Molony, S. B. (2) Accel. from. See Dithiocarbamates.

#### **Benzaldipiperyl.**

Bayer & Co. (5) (6) (9) (13) & (14) An accel. of vulc. Also used in synth. R.

Twiss, D. F. (2) An accel.

#### **Benzalpiperyl.**

Bayer & Co. (5) (6) (9) & (14) An accel. of vulc.

#### **Benzidine.**

Bayer & Co. (41) See Ageing-Tackiness.

Cadwell, S. M. (3) See Aldehyde-Amines.

Gottlob, K. O. (8) A weak accel. for Synth. R.

Kratz, G. D., Flower, A. H. & Shapiro, B. J. (1) See Aniline.

Weber, C. O. (9) Discoloration during cure very common in fabrics dyed with benzidine dyestuffs.

**Benzoflavine.**

Gaisman, L. & Rosenbaum, J. L. (1)  
An accel. of vulc.

**Benzol.** See Poisoning.

**Benzoquinone.**

Peachey, S. J. (26) An accel. of vulc.  
of R. by  $H_2S$  and  $SO_2$ . Peachey  
process.

**Benzoyl-disulfide.**

Cadwell, S. M. (1) (5) & (6) See  
Xanthates.

**Benzoyl-butyl-xanthogenate.**

**Benzoyl-ethyl-xanthogenate.**

Cadwell, S. M. (7).

**Benzoyl peroxide.**

Ostromuiskii, I. (11) Vulc. of R.  
with this peroxide is retarded by resins  
or amines. Proteins increase tensile  
and extensibility. (14) & (31) Will  
vulc. R. at ordinary temp. after pre-  
liminary warming at  $30^{\circ}$ - $80^{\circ}$  C.  
Oxides are unnecessary and produce  
poor quality. (27) R-20, peroxide-4.  
Cure 15 min. at 30 lbs. (30) Vulcan-  
izing agent of R.

**Benzylamine.**

Anon. (84) An accel.  
Bayer & Co. (19).  
Cadwell, S. M. (3) See Aldehyde-  
Amines.  
Ditmar, R. (62) A rapid accel. of vulc.  
Dubosc, A. (30). (40).  
Eaton, B. J. (8).  
Ostromuiskii, I. (17) As effective  
an accel. as an aliphatic amine.

**Benzyl-m-phenylenediamine.**

Bayer & Co. (41) See Ageing-Tack-  
iness.

**Benzyl ether.**

Bayer & Co. (38) Increase of elas-  
ticity of vulc. R. by use of 5-8% of  
aryl or aralkyl ethers such as benzyl  
ether or dixyl ether.

**Benzyl-ethylamine.**

Maximoff, A. (1)  $CS_2$  reaction product  
is a powerful accel.

**Benzylidene-aniline.**

Peachey, S. J. (2) R-100, S-10, accel.-1.  
Cure 40 min. at  $140^{\circ}$  C.

Twiss, D. F. & Brazier, S. A. (1) An  
accel.

**Benzylidene-ethylamine.**

Peachey, S. J. (2) An accel. of vulc.

**Benzylidene-tertiary-amylamine.**

See  
Amylamine.

**Biguanide.** See Guanyl-guanidine.

**Bismark Brown.**

Dubosc, A. (30).  
Gaisman, L. & Rosenbaum, J. L. (1).  
Marzahn, R. (1) p. 80. Should never  
be used in R.  
Weber, C. O. (1) One of numerous  
coloring materials injurious to R.

**Bismuth Carbonate.**

Pilkington, W. (1) Cold solution of bis-  
muth carbonate restores resiliency  
and prevents cracking of R.

**Bismuth Iodide (bromide).** See Anti-  
mony Iodide.

**Bismuth Nitrate.**

Goodyear, Chas. (5) See Nitric Acid.

**Bismuth Polysulfide.**

Harris, C. T. (1) Vulc. of R. at  $210^{\circ}$   
F. by bismuth polysulfide with white  
lead in absence of free S.  
Pickles, S. S. (4).  
Turner, W. A. (2) First to use mix-  
ture of  $BiS$  and  $PbS$ . R-3,  $BiS$  and  
 $PbS$ -1. Cure at  $138^{\circ}$ - $142^{\circ}$  C. Prod-  
uct does not become hard and brittle  
on heating at  $200^{\circ}$  C.

**Bitumen.**

Smith, J. (1) See Ageing-Oxidation.

**"Black Hypo."** See Lead Thiosulfate.

Weber, C. O. (61) p. 183-5. Black  
hypo is a mixture of lead carbonate,  
sulfide, thiosulfate, and sulfate with  
free S.

**Bloom.** See Sulfur-Bloom.

**Bone oil.**

Murrill, P. I. (2) Patented as an accel.  
of vulc. (5) Mentioned.  
Tassilly, E. (1) p. 232. One of the  
first solvents found for R.

**Borax.** See Latex-Synthetic.

- Boric Acid.** See Latex-Preservatives.  
 Eaton, B. J. (16) Soaking fresh coagulum in boric acid retarded the cure.  
 (23) See Tannin.
- Bornesite.** See Dambonite.  $C_{14}H_7O_{11}$   
 m.p.  $175^{\circ}$  C. Sublimes  $205^{\circ}$  C.  
 Girard, A. (1b) Found in Borneo R.
- Bran.** See Sawdust.
- Bromine.**  
 Anon. (117) Bromination of vulc. R.  
 (130) Action of Br on R. facilitated by sulfuryl chloride.  
 Blossom, T. M. (1) Action of halogens on R.  
 Budde, Th. (3) Action of Br on vulc. R. and its application in analysis.  
 Caspari, W. A. (1) Br acts on gutta percha. Product darkens at  $130^{\circ}$  C. with evolution of HBr. (3) Bromination of R. containing varying amounts of combined S.  
 Eduardoff, F. (1) Action of Br on resins in latex. (2) Action on latex.  
 Gerner, H. (2) R. dipped in Br is instantly vulc.  
 Gladstone, J. H. & Hibbert, W. (1) Action on R.  
 Gottlob, K. O. (6) p. 97. Vulcanizes R.  
 Herbst, E. & Stern, R. (1) Action on R.  
 Hinrichsen, Quensell & Kindscher. (1) See Chlorine.  
 Hübener, G. (2) Bromine water converts ebonite dust to bromide derivative.  $CS_2$  will separate the crude R. tetrabromide from the brominated vulc. R. (3) Analysis of vulc. R. (8) 77% of S in ebonite is oxidized to  $H_2SO_4$  by Br. (9) Bromination of vulc. R. (13) Bromination of methyl rubber.  
 Kirchhof, F. (2) Quantitative measurements of the additive reactions of R. R. and Br at  $18^{\circ}$  C. give  $C_{10}H_{16}Br_2$ . This heated at  $80^{\circ}$  C. loses HBr to  $C_{10}H_{14}Br$ . (3) Regeneration of R. from its tetrabromide. (6) See sulfuric acid.  
 Lichtenberg, O. (1) Action of Br on R. regenerated from the ozonide.  
 Marzahn, R. (1) p. 93. Br in mixture of turpentine and  $H_2SO_4$  will vulc. R. to ebonite.  
 Newbrough, J. B. & Fagan, E. (1) Treating R. with a mixture of Br and I with heat. (2) Treatment of R. articles with Br. (4) See Iodine.  
 Ostromuiskenskii, I. (1) Regeneration of R. from its bromide. Sodium reduces the bromide in  $C_6H_5Cl$ , containing trace of ether, with explosive violence. Zinc dust also used. (7) Conversion of vinyl bromide into the bromide of erythrene caoutchouc. (10) Action of halogens on R. is not accompanied by depolymerization of the molecule. R. bromide has no properties in common with dimethyl cyclooctadiene tetrabromide. (26) R. bromide used as a vulc. agent for fresh R. See Chlorinated rubber.  
 Parkes, A. (1) Vapor cures with Br.  
 Pearson, H. C. (1) p. 64.  
 Pickles, S. S. (2) R. absorbs 4 atoms of Br and remains a complex molecule.  
 Ramsay, Chick & Collingridge. (1) Action on gutta percha.  
 Schmitz, W. C. (2) Absorption of Br is complete at 5 atoms of bromine. (4) Constitution of R. determined by the use of Br.  
 Seeligman, Torrillon & Falconnet. (1) p. 132 & 163. Acts on R. like S but more energetically.  
 Spence, D. (17) Action of Br on R. proteins.  
 Staudinger, H., Muntwyler, O. & Kupper, O. (1) Action of Br on isoprene.  
 Vaubel, W. (1) R. absorbs 6 atoms of bromine, 4 additive and 2 substitutive. Influence of resins and proteins is not known.  
 Vaubel, W. & Wienerth, E. (1) Action of Br on R.
- Brom-iodide.**  
 Gottlob, K. O. (6) p. 97. Acts as a vulc. agent of R.
- Brucine.**  
 le Blanc, M. & Kröger, M. (1) See Viscosity.
- "Burnt Hypo."** See Lead Hyposulfite.
- Butyl Alcohol.**  
 Twiss, D. F. (6) Na or K hydroxide dissolved in butyl alcohol as an accel. of vulc.
- Butyl Aldehyde.** See Aldehyde-Amines.

**Butylene.**

Bouchardat, A. (1) See Distillation of Rubber.

**Butyl Dithiocarbamates.**

Molony, S. B. & Nikaido, Y. (1) (2) See Dithiocarbamates.

**Butyl oxyester of potassium thiolcarbonate.**

Cadwell, S. M. (5) & (6) An accel.

**Butyl thiocarbonic acid disulfide.**

Cadwell, S. M. (2). (5). (6). See Xanthates.

**Butyl Xanthates.**

Cadwell, S. M. (1). (5). (6) See Xanthates.

**Butyl aldehyde aniline.**

**Butyl aldehyde aniline, (iso-).**

**Butyl aldehyde diethylamine.**

**Butyl aldehyde monoethylamine.**

**Butyl aldehyde p-toluidine.**

Cadwell, S. M. (3) See Aldehyde-Amines.

**Cadmium Sulfide.**

Anon. (178) An accel. Non-poisonous. (220) No effect on elasticity or durability. An accel. of vulc.

Breuil, P. (13) No effect on elasticity or strength of R. Accel. of vulc. Non-poisonous.

Lascelles-Scott, W. (32) Accel. of vulc.

**Cadmium Xanthates.**

Cadwell, S. M. (2) See Xanthates.

**Calcium.** See Sodium.

Esch, W. (10) Used for devulcanization of R.

Kirchhof, F. (3) See Tetrabromide.

**Calcium Bisulfite.**

**Calcium Sulfite.**

Heilbronner, A. (1) See Tannin.

Zingler, M. (1) & (2) See Ageing-Tackiness.

**Calcium Carbonate (chalk).**

Breuil, P. (8) Increases strength and extensibility of R.

Ditmar, R. (11) Chalk enters into colloidal combination with R. and does

not react with S. Chalk is binder of moisture during vulc.

Herbst, E. (2) Chalk in vulc. R. is dissolved out by dil. acids.

Lascelles-Scott, W. (27) Pure R., and vulc. R. to even a greater degree, deteriorate in presence of whitening.

Williams, H. J. (1) Pt. I. Manufacture and use of whitening and Paris white.

**Calcium Chloride.** See Latex-Coagulation.

Anon. (266a) See Variability.

Breuil, P. (8)  $\text{CaCl}_2$  in presence of sulfur produces a sulfide and chlorine. The chlorine and sulfur form sulfur chloride, which acts on the rubber. In water the sulfur chloride is decomposed and does not act harmfully on R.

Tour du Breuil, H. M. F. Graf de la. (1) Vulc. in solution of  $\text{CaCl}_2$ .

Vernet, G. (6) The rôle of calcium in coagulation. See Latex-Coagulation.

Whitby, G. S. (1)  $\text{CaCl}_2$  has marked influence on tendency to oxidation.

**Calcium Hydroxide.** See Lime.

**Calcium Hypochlorite.** See Hypochlorites.

Breuil, P. (8) Used by Claubry for vulc. in cold.

Claubry, H. G. de. (1)  $\text{S}_2\text{Cl}_2$  replaced with mixture of calcium hypochlorite and S as vulc. agent for R.

**Calcium Oleate.**

Dannerth, F. (1) An accel. of vulc.

**Calcium Oxide.** See Lime.

**Calcium Malate.**

Henke, G. (1) Present in 21 species of Euphorbia examined.

**Calcium Pentasulfide.**

**Calcium Sulfide.**

Bourquin, H. (1) Vulc. of R. with polysulfides of hydrogen, sodium and calcium.

Clouth, E. (1) p. 137.

Gerard, A. (1) Vulc. R. goods in a  $25^\circ$  Be. solution of  $\text{CaS}_2$  at  $140^\circ \text{C}$ .

Graham-Otto. "Lehrbuch der Chemie." Vol. 3, Sec. 2, p. 382.

Heinzerling, C. (1) p. 64. Gutta percha—48,  $\text{CaS}$ —6 used by C. Hancock in



1847. 10-15% CaS or BaS with R. gives good vulcanization at 132°-145° C.
- Marzahn, R. (1) p. 270. Describes A. Gerard's method of vulc.
- Moulton, S. (2) Use in R.
- Ostromuiskii, I. (17) CaS<sub>2</sub> is a vulc. agent of R.
- Pearson, H. C. (1) p. 64.
- Spence, J. B. (1) See Polysulfides.
- Calcium Stearate.**  
Dannerth, F. (1) An accel.
- Calcium Thiosulfate.**  
Levinstein, E. (1) Will vulc. R. without S.
- Calcium Trithiocarbonate.** See Trithiocarbonates.
- Calcium Xanthates.**  
Cadwell, S. M. (1) (2) (4) (5) & (6)  
See Xanthates.
- Camphor.**  
Anon. (193) See Latex-Preservatives.  
Gerner, H. (1) Use of camphor in R.
- Canada balsam.**  
Anon. (69) See F. Wilhöft (1).  
Wilhöft, F. (1) Balsams heated with S give a compound which when compounded into R. holds the S in a non-blooming form. See Sulfur-Bloom.
- Caoutschen.**
- Caoutchene.** See Distillation of Rubber.  
Bouchardat, A. (1) Melts at -10° C. Boils at +14.5° C./752 mm.  
Ramsay, Chick & Collingridge. (1).  
Williams, G. (1) Formed by destructive distillation of gutta percha.
- Caoutschin.**
- Caoutchine.** See Distillation of Rubber, Kautchin.  
Camille, A. (11) A solvent for R.  
Himly, C. (1) C<sub>2</sub>H<sub>4</sub>. Fraction from dry distillation of R. from 140°-280° C. b.p. 171.5° C.
- Caoutchecine.** See Distillation of Rubber.
- Caoutchene.** See Distillation of Rubber.
- Caoutchouc.**  
Geer, W. C. (5) p. 5. "Caoutchouc" means "Weeping Tree."
- Caoutchoucine.** See Distillation of Rubber.  
Schidrowitz, P. (25) Suggested as a denaturant for alcohol.
- Caoutchukin.** See Distillation of Rubber.
- Carbanilide.**  
Bedford, C. W. (1) Active accel. at temp. of 60 lbs. steam but not at 40 lbs.  
Ricard, E. (2) Mentioned.
- Carbo-diphenyl-diimide.**  
Schidrowitz, P. (19) Not an accel.  
Twiss, D. F. & Howson, C. W. H. (1) Not an accel.
- Carbon.** See Gas Black, Lamp Black.  
Dannerth, F. (4) Discussion of various forms of carbon as R. pigments.  
Lascelles-Scott, W. (25) Lamp Black as a R. pigment.  
Rose, R. P. (1) Activated carbon for use in R.
- Carbon Dioxide.** See Ageing-Tackiness, Depolymerization, Gases, Light.  
d'Arsonval. (1) CO<sub>2</sub> passes thru R. very rapidly.  
Edwards, J. D. & Pickering, S. F. (1) Permeability thru R.  
Heurn, F. C. van. (1) Heating R. in CO<sub>2</sub> at 130° C. improves it. Extensibility of vulc. R. is increased. Presence of O<sub>2</sub> is detrimental.  
Kogakushi, K. (1) See Ageing-Tackiness.  
Radt, V. (1) CO<sub>2</sub> not absorbed by R. to any appreciable extent. Diffusion of CO<sub>2</sub> thru R. due to its solubility in water and "hygroscopic nature" of the R.  
Rossem, A. van. (6) R. heated 4 hrs. in CO<sub>2</sub> will vulc. faster than before.
- Casein.** See Protein.  
Biddle, A. (1) Add. of casein to latex prior to coagulation. Use of 10% in R. mix.  
Dubosc, A. (23). (30). (26) Reacts with S to form H<sub>2</sub>S during vulc.  
Eaton, B. J. & Grantham, J. (4) Casein fermented in air is a weak accel. Fer-

- mentation in absence of air produces a strong accel.
- Frood, F. & Alger, H. P. (1) Fire proofing R.
- Skellon, H. (1).
- Stevens, H. P. (2).
- Castor Oil.**
- Weber, L. E. (9) Rancid castor oil is an accel. See Oleic Acid.
- Caustic.** See Alkali, Sodium Hydroxide, etc.
- Celluloid.**
- Jones, F. (1) Admixture with R.
- Cellulose.**
- Lascelles-Scott, W. (18) Precipitated cellulose accelerates process of vulc. with S and  $S_2Cl_2$ .
- Cellulose Xanthate.** See Xanthates.
- Brown, H. E. & Stover, J. H. (1) R. vulc. by admixture with cellulose xanthate and heating.
- Collardon, L. (1) Cellulose xanthate is added to R. prior to vulc.
- Ceresin.**
- Ahrens, P. (5) See Ageing-Oxidation.
- Anon. (286) Used in R. mixings to render them resistant to oxidation.
- Bradley, W. P. (1) See Ageing-Oxidation.
- Britland, W. J. & Potts, H. E. (1) Ceresin has beneficial effect on ageing of R. by keeping resin content lower.
- Grossman, F. (1) See Ageing-Oxidation.
- Himmelbauer & Co. (1) R. articles dipped in melted ceresin.
- Hinrichsen, F. W. & Kindscher, E. (2) Ceresin increases acetone extract of R. (3) Resin content of vulc. R. increased by ceresin.
- Revere Rubber Co. (1) See Ageing-Oxidation.
- "Chatterton's Compound."**
- Obach, E. F. A. (1) J. S. C. I. 17,474 (1898) A mixture of gutta percha, rosin and Stockholm tar for use in cables.
- Chinin.** See Quinoline.
- Blanc, M. le & Kröger, M. (1) See Colloid chemistry of rubber.
- Chinolin.** See Quinoline.
- Chinosol.** See Quinoline, Quinosol.
- Chlor-bromide.** See Bromine, Chlorine.
- Anon. (130) Chlor-bromide derivative of R. soluble in benzol and toluol.
- Chlorhydrin.**
- Hütz, H. (1) See Regeneration.
- Chloride of lime.**
- Claubry, H. G. de. (1) See Sulfur Chloride.
- Chlorine.**
- Chlorinated rubber.**
- Anon. (36) & (52) "Duroprene," Peachey's chlorinated R. (130) Chlorination of R., balata, or gutta percha in suitable solvents.
- Bedford, C. W. & Kelly, W. J. (1) Chlorination of R. which has been vulc. with S,  $S_2Cl_2$  or etc.
- Berzelius, J. J. (1)  $Cl_2$ ,  $Br_2$ ,  $I_2$ ,  $SO_2$ , HCl, fluosilicic acid, fluoboric acid, and  $NH_3$  do not attack R. (1835).
- Broadhurst, H. M., Lamble, A. & Peachey, S. J. (1) Use of chlorinated or brominated R. as a plastic mass.
- Bronde, W. T. (1)  $Cl_2$ ,  $Br_2$  and alkalis do not attack R. (1848).
- Brooks. (1) p. 123.
- Camille, A. (7)  $Cl_2$  passed into R. solution.  $NH_3$  then passed in to remove excess. Forms ivory or ebonite substitute.
- Caspari, W. A. (1) Halogen derivatives of gutta percha, balata or R. are chemically inert. Heated with sodium ethylate they give oxygen compounds which are not halogen free.  $Cl_2$  on gutta percha gives product that is plastic below  $100^\circ C$ .
- Ditmar, R. (22) Action on balata. (47) Chlorine, bromine and iodine derivatives of R.
- Edison, T. A. (1) Chlorinated R. or balata and mixtures of R. with chlorinated R. as covering for electric wire.
- Englehard, G. A. & Day, H. H. (1)  $Cl_2$  on R. or gutta percha gives white hard product. (1859).
- Englehard, G. A. & Havemann, R. F. H. (1)  $Cl_2$  on R.
- Gerner, H. (2)  $Cl_2$  as a vulc. agent of R.

- Gladstone, J. H. & Hibbert, W. (1) Action of  $\text{Cl}_2$  on R. Best specimen chlorinated R. contained 65.18% Cl corresponding to the formula  $\text{C}_{10}\text{H}_{14}\text{Cl}_8$ .  $\text{HCl}$  was given off. (1888).
- Havemann, R. F. H. (1)  $\text{Cl}_2$  on R. and gutta percha gives white hard product. Mixed with  $\text{ZnO}$  or lime gives an ivory like product.
- Heinzerling, C. (1) p. 29.  $\text{Cl}_2$  gas reacts vigorously on R. changing it to a hard, brittle product.
- Helm, J. (1) A white hard R. by adding liquid chlorine to R.
- Herbst, E. & Stern, R. (1) Action on R.
- Hinrichsen, F. W. (8) Action on R.
- Hinrichsen, F. W. & Kempf, R. (1) Prepared  $\text{C}_{10}\text{H}_{14}\text{Cl}_8$  derivative of R. in  $\text{CHCl}_3$  solution.
- Hinrichsen, F. W., Quensell, H. & Kind-scher, E. (1) Prepared  $\text{C}_{10}\text{H}_{14}\text{Cl}_8$  derivative of R. by passing dry  $\text{Cl}_2$  into ice cold solution of R. in  $\text{CHCl}_3$ .
- Hurtzig, F. & Hurtzig, Th. (1) Chlorination of R. or gutta percha in  $\text{CHCl}_3$ ,  $\text{CS}_2$ ,  $\text{C}_6\text{H}_6$  or turpentine solution of R. Also by immersing thin strips of R. in saturated solution of chlorine water. Addition of metallic oxides, etc., to make ivory substitutes. (1865).
- Lamble, A. (1) "Duroprene." Chlorinated R. made under Peachey patents by United Alkali Co.
- Ostromuiskii, I. (18) Action of chlorine on R. Vulc. of R. by the halides of R. (20)  $\text{Cl}_2$  converts R. into an ebonite like material—stable to acids, alkalis and high temperatures. (23) Chlorides of natural, isoprene and erythrene caoutchouc. (26) Halogenated R. will vulc. R. to a soft or hard product. R.-10, R. bromide-7. Cure 90 min/130° C. to ebonite.
- Peachey, S. J. (6) Patent on heptachloride of R. Action of mixed  $\text{Cl}_2$  and  $\text{Br}_2$  on R. (7) Preparation of a plastic by chlorinating R.
- Pearson, H. C. (1) p. 64-5.
- Rodier, P. (1)  $\text{Cl}_2$  gas passed into cooled mixture of  $\text{NH}_4\text{Cl}$  and sulfuric acid chlorhydrin to saturation. Neutralize with  $\text{CO}_2$ . Mix with R. or oil and vulc. at 60° C.  $\text{Na}_2\text{S}$  accelerates this method of vulc.
- Seeligmann, T., Torrilhon, G. L. & Falconnet, H. (1) p. 162. Acts like S on R. but more energetically. p. 118 & 163.  $\text{Cl}_2$ ,  $\text{Br}_2$  or  $\text{I}_2$  added to Hevea latex cause darkening to brownish color and agglomeration to a ductile mass. Action more energetic on R. itself.
- Siemens, C. & Halske. (1) Reduction of halogenated or hydrohalogenated R. by metals (Zn) to give gutta percha like products.
- Thenard, L. J. (1)  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ ,  $\text{SO}_2$ ,  $\text{HCl}$ , fluosilicic acid, fluoboric acid, and  $\text{NH}_3$  do not attack R. (1835).
- Thomson, W. (6) Halogen addition products of R. are distinguished from ordinary vulc. R. by solubility, stability, and sensitiveness to temperature changes.
- Ure, A. (3) Neither  $\text{Cl}_2$ ,  $\text{SO}_2$ ,  $\text{HCl}$  (gas),  $\text{NH}_3$  or fluosilicic acid affect R.
- Warren, T. T. P. B. (1) Claims discovery of vulc. of R. by halogens. (1871). See Iodine.
- Weber, C. O. (14) Action on R.
- Wildermann, M. (1) Ebonite resistant to chlorine.
- Chlorogenic Acid.**
- Gorter, K. (5) Present in latex of *Cassipoula elastica* and *Ficus elastica*.
- Chloronaphthalene.**
- Aylsworth, J. W. (1) Softens R. and aids vulc.
- Condensate Co. of Am. (1) Chlorinated naphthalenes facilitate action of S on R.
- Chlorophyll.**
- Repony, D. (2) Used as a R. pigment. See Dyes.
- Cholesterin.**
- Cholesterol.**
- iso-Cholesterol.**
- Cohen, N. H. (2) Identified beta-amyirin acetate and isocholesterol in resin of Euphorbia R. Differs from cholesterol in that it is dextro rotatory.
- Dubosc, A. (3) Jelutong R. resin contains isomers of phytosterin or plant cholesterin, which are related to cholesterol. (14) Cholesteryl stearate present in R. resins.
- Hillen, G. H. (1) Isocholesterol acetate found in resin of *Manihot glaziovii* of German East Africa.

- Hutchinson, A. (1) R. or gutta percha combined with lanolin at 212° F. (2) R. removes lanolin from boiling solution of wool grease and caustic alkali.
- Chromates.**  
 Anon. (178) See Ageing. (266a) See Variability.  
 Bernstein, G. (6) See Lead Sulfide.  
 Lascelles-Scott, W. (32) Action on R.  
 Ostromuiskii, I. (11) & (19) See Ageing-Oxidation.
- Chromic Acid.**  
 Anon. (178) In weak sol. does not affect R.  
 Lascelles-Scott W. (32) Pure chromic acid in aqueous solution is less destructive to pure R. than when the substances are impure.
- Chromic Oxide.**  
 Lascelles-Scott, W. (36) Chemically inert and without effect on R. Best green inorganic pigment. Other chromium pigments.  
 Weber, C. O. (9) Harmless to R. in waterproof goods.
- Chromium Dithiocarbamates.**  
 Molony, S. B. & Nikaido, Y. (1) & (2) See Dithiocarbamates.
- Chromogenic Organisms.** See Enzymes.
- Chromyl Chloride.**  
 Spence, D. & Galletly, J. C. (1) Action on R. gives  $C_{10}H_{16}(CrO_2Cl_2)$ . Insol. in organic solvents.
- Cinconina.**  
**Cinchonine.**  
 Eaton, B. J. & Bishop, R. O. (1) See Quinoidine.
- Cinnamaldehyde.** See Aldehyde-Amines.
- Cinnamaldehyde aniline.**
- Cinnamaldehyde monoethylamine.**  
 Cadwell, S. M. (3) See Aldehyde-Amines.
- Cinnamic acid.**  
 Frank, F. & Gnaedinger, J. (1) Present in Kickxia latex.  
 Ostromuiskii, I. (13) Aids in vulc. of synth. R.  
 Tschirch, A. & Schereschewski, E. (1) See Balata.
- Citronellal.** See Aldehyde-Amines.
- Citronellal Aniline.**  
 Cadwell, S. M. (3) See Aldehyde-Amines.
- Coagulation.** See Latex-Coagulation.
- Coal tar.**  
 Dittmar, R. (37) Influence of coal tar on steam cure and on oxidation of R.
- Cobalt amines.**  
 Dubosc, A. (15). (24). (34) Used with ZnO as accel. of vulc.
- Cobalto-ammonium-trithiocarbonate.** See Trithiocarbonates.
- Cold. Effect on R.**  
 Anon. (70) R. on cooling becomes as brittle as glass. (141) at temp. of liquid air, R. crumbles readily. (244) Effect of low temp. on R. articles.  
 Breuil, P. (15) See Heat.  
 Dewar, J. (1) Properties of R. cooled to -252° C.
- Cold vulcanization.** See Sulfur chloride, Dithiocarbamates, Xanthates, Dithioacids, Peachey Process, Vulcanization at low temperatures.
- Colloid Chemistry of Rubber.** See Ageing - Tackiness, Depolymerization, Rubber-Chemistry of, Viscosity, Latex-Synthetic.
- Ahrens, F. (2) Polemical with Spence on cause of tackiness and changes in viscosity. "Para spots" in pure vulc. R. consist of an organic substance and not of crystals of S. (6) Blooming. Loss of S on ageing. Reversibility of vulc. process. S must be present in something more than mechanically dissolved state.  
 Anon. (101) See Latex.  
 Bancroft, W. D. (1) Two surfaces of unvulc. R. unite very readily, it should follow that vulc. R. adsorbs air more strongly.  
 Bary, P. (2) Behavior of R. with solvents.  
 Blanc, M. le & Kröger, M. (1) Vulc. of R. in solution with and without accel. by use of S,  $S_2Cl_2$ ,  $H_2S$  plus  $SO_2$  etc. Vulc. measured by viscosity and gel formation. See Viscosity for list of accels. tested.

- Caspari, W. A. (4) Osmotic properties and physical constitution of R. solutions. (5) Composite nature of raw R. (6) The systems R.-benzene-alcohol and R.-benzene-acetone.
- Ditmar, R. (7) Colloidal action of R. on selenium. (8) R. is a highly polymerized product intermediate between the aliphatic and aromatic terpenes. R. partly soluble in ether and this part is almost free from oxygen. (12) The higher the resin content of R. the more easily it swells in CS<sub>2</sub>. Masticated R. swells more rapidly than dry raw para R. Warmth accelerates swelling but retards solution. The higher the degree of polymerization the greater the elasticity. (13) Swelling of masticated para R. in various solvents. (46) Chalk is a colloidal compounding ingredient for R. (48) Shrinkage spots on R. (51) "Para spots" due to previous history of the R. and varying size of globules in latex. Para R. is a "polycoagulase system" in which micro and macro coagula have different vulc. coefficients which may be detected by the different colors, hence the spots. (63) See Ageing.
- Ditmar, R. & Thieben, R. (2) Shrinkage spots due to local rapid combination of S.
- Dubosc, A. (7) See Vulcanization-Theories. (16) & (57) Colloidal nature of R. (21) Action of solvents on R.
- Flamant, G. (1) Abnormal amounts of protein in Congo R. The R. is held in suspension by the proteins. The lower the protein the easier spontaneous coagulation takes place. These proteins increase tackiness.
- de Fleury, R. (1) Application of physical chemistry to explain the properties of R.
- Hinrichsen, F. W. (1) Review of researches and physical-chemical studies on R.
- Höhn, J. B. (1) Vulc. with S due to absorption of S by R. and not to chemical action. S<sub>2</sub>Cl<sub>2</sub> separates S very easily and this is the S that affects vulc.
- Kirchhof, F. (4) Swelling of vulc. R.
- Kohlschütter, V. (1).
- Lewis, E. W. & Walmsley, H. (1) A strip of Pb immersed in a soln. of R. in benzene containing CS<sub>2</sub>. Pb slowly passes into solution. Traces of alcohol hasten it. PbS is said to be held in colloidal solution under protective influence of R.
- Liesegang, R. E. (1) Cu oleate easily passes through vulc. R. whereas sugar, AgNO<sub>3</sub> and LiCl do not, showing that membranes do not act as sieves.
- Minder, J. (5) The nature of R. A discussion.
- Netherlands Government Institute. (3) R. present in latex in as high a degree of polymerization as in the R. obtained by coagulation.
- Ostromuiskii, I. (5) Definition, classification, evaluation of R. "Temperature of elasticity." "Dead temperature."
- Ostromuiskii, I. & Kelbasinskaya, I. M. (1) Physical constants of solutions of various rubbers in various solvents.
- Ostwald, Wo. (1). (2).
- Ostwald, Wo. & Fischer, M. H. (1) p. 191 & 200. J. Perrin found that add. of acids to gutta percha suspensions has no "appreciable influence on their brownian movement." Henri, V. found that the brownian movement of rubber latex was reduced one-half by N/10 NaOH and one-ninth by N/32 HCl.
- Ostwald, Wo. & Wolski, P. (1) HgS sols. in alcohol do not pass thru R. membranes.
- Poschl, V. (1) Protective colloid action of proteins and peptones in latex is broken up by dilution or chemical reagents. Vulc. is an adsorption of the vulc. agent with subsequent chemical action.
- Posnjak, E. (1) "Über den Quellungsdruck."
- Pott, H. (1) Present status of colloid chemistry and its relation to R.
- Rechyler, A. (3) CO<sub>2</sub> and SO<sub>2</sub> absorption by R. is only a case of solution.
- Schidrowitz, P. (1) R. globules are not destroyed by coagulation. They exist in the dry R. and are not removed by solution in benzene.
- Schulze, E. (1) CS<sub>2</sub>, benzene or naphtha do not give true solutions with R. The R. swells in them and is

- partially dissolved and forms an emulsion with the solvent.
- Skellon, H. (3) See Sulfur.
- Spear, E. B. (1) Discussion of condensation, polymerization, crystallization, coagulation and gelation and their relation to R. Selective adsorption of the pigments by R. is cause of increase in tensile strength.
- Spence, D. (18) Loss of viscosity of R. solution exposed to light for a very short time is due to a physico-chemical change of the R. rather than oxidation. (19) Extraction data on removal of free S.
- Spence, D. & Scott, J. H. (2) Physico-chemical investigations of the resin extraction process.
- Stevens, H. P. (22) Action of solvents on vulc. R. (45) Vulc. of R. in sol and gel forms. (73) Review of the colloid chemistry of R. with bibliography. Effect of vulc. on dispersion of pigments.
- Twiss, D. F. (10) R. as a colloid. (11) Sols and gels of vulc. R.
- Wagner, A. (1) Spots on the surface of R. are due to crystallization of S.
- Weber, C. O. (39) Mixing colloidal materials into R. by emulsifying them in the R.
- Weil, R. (1) Colloid chemistry of latex. Brownian movement. Syneresis. Swelling in solvents. Viscosity. Oxidation and tackiness. Sc in hard and soft R. Vulc. is not reversible. Accelerators. Vulc. with  $S_2Cl_2$  or  $H_2S$  and  $SO_2$ .
- Zsigmondy, R. & Spear, E. B. (1) Theories of coagulation and vulc.
- Colophony (rosin).**
- Ostromuiskii, I. (13) Used in synth. R. (22) Resins, balsams, and tars (rosin) used with  $ZnO$  or other oxides to aid S cures. Organic accel. may or may not be used. Hexa. piperidine-pentamethylene-dithiocarbamate and zinc menthyl-xanthate are mentioned. Menthol, terpineol or geraniol also active in presence of oxides.
- Stevens, H. P. (2) Without effect on vulc. of R.
- Compounding Ingredients.**
- Anon. (97)  $MgCO_3$  as a compounding ingredient in R. (133) Diatomite as a substitute for  $MgO$ , as a compounding ingredient but not as an accelerator. (257) Carbon and gas blacks. Analysis for fineness. Use in R.
- Bayer & Co. (27) Condensation products of aralkyl-halides such as benzoyl-chloride, xylyl-chloride or p-xylylene-dichloride with naphthalene, phenathrene, anthracene, xylene, benzene, cymene, etc.
- Beadle, C. & Stevens, H. P. (4) Influence of  $ZnO$ ,  $MgO$ , and talc on the physical characteristics of vulc. R.
- Breuil, P. (6) Lithophone a fine pigment with good covering power. Unaffected by  $H_2S$ . (14) Carbonized shale, graphite, vegetable blacks, smoke blacks and animal charcoal in R.
- Ditmar, R. & Thieben, R. (1)  $MgCO_3$ ,  $MgO$ ,  $CaO$ ,  $ZnO$ ,  $BaSO_4$ ,  $PbO$ , and  $CaCO_3$  heated in an autoclave with S vapor at 4 atm. They were partially or wholly converted to sulfides or sulfates.
- Eaton, B. J. & Grantham, J. (3) Variability of R. with different technical mixings.
- Heinzerling, C. & Pahl, W. (1) Effect of mineral admixtures on soft and hard rubber and on gutta percha. All mineral and organic admixtures diminish the elasticity of soft R. In soft R. the resistance to stretching is increased by pitch, chalk, heavy spar,  $ZnO$  and  $MgO$ . Vermillion and  $MgO$  have the same effect in hard rubber.  $PbO$  and hydrated lime diminish resistance to stretching of soft and hard rubber. Most mixtures containing metallic oxides are attacked by acids.  $PbO$  and  $ZnO$  increase oil resisting property. Most mineral and R. mixtures become hard in time.
- Lascelles-Scott, W. (33) & (34) Blue pigments for R. Cobalt blue colors. Mountain blue, a copper compound not good for R. Prussian blue not stable enough. Ultramarine. Molybdenum blue.
- Marckwald, E. & Frank, F. (12) Lamp-black in R. mixings.
- North, C. O. (2) Comparative effect of barytes, tripoli, lithophone,  $MgCO_3$ ,  $ZnO$ , and gas black on physical properties of R.
- Pickles, S. S. (3) Lecture on "fillers."

- Rose, R. P. (1) Activated carbon black for use in R.
- Schippel, H. F. (1) Volume increase of compounded R. under strain.
- Spear, E. B. & Endres, H. A. (1) Obscuring power diminishes with reduction of particle size as molecular dispersion is reached. Maximal obscuring power may correspond to maximal compounding effect. Too low a particle size may reduce stiffening action too greatly.
- Stevens, H. P. (3) Function of PbO.
- Stitt, C. (1) Pigments and colors used in R.
- Toch, M. (1) Properties of R. pigments.
- Wiegand, W. B. (1) Change in physical properties of R. with increasing amounts of various pigments.
- Constitution of Rubber.** See Rubber-Structure and Chemistry.
- Copal.**
- Hutin, A. (1) See Shellac.
- Copper.** Metal, oxides, salts, etc.
- Anon. (36) See Ageing-oxidation. (73) Review of Burghardt (1). (169) Cu wire is tinned before coating with R. to prevent deterioration. (225) See Dyes. (285) Cu deteriorates R. rapidly, especially in the presence of fats or oils.
- Asano, K. (1) Cu accelerates tackiness in R. by depolymerization and not through oxidation.
- Bing, K. (1) Traces of Cu or Cu salts greatly accelerate the deterioration of R.
- Burghardt, C. A. (1) On the alteration of R. in air.
- Camille, A. (7) & (11) Cu causes oxidation of R. Pt has slight action. Zn and Ag have no action.
- Dewar, J. (1) Metallic Cu exerts strong oxidizing effect, Pt very slight, while Zn and Ag have no harmful effect. Tests at 150° F.
- Ditmar, R. (62) Black CuO gelatinizes R. and retards vulc. Red Cu<sub>2</sub>O hardens R. on the mills and greatly shortens the cure.
- Dubosc. A. (30) Black Cu oxide does not affect the rate of vulc. Red Cu oxide is a strong accel. 1% gives 30 min. cures and turns the R. green. (35) Cu salts are introduced into R. thru the acetic acid used in coagulation.
- Esch, W. (11) Cu catalyzes oxidation and formation of acid in R.
- Fickendey, E. (1) Cu and Fe accel. the oxidation of R.
- Fox, C. P. (1) Cu acetate causes tackiness in R. Ammonia copper salts have a pronounced hardening effect on R. Cu salts increase the deleterious effect of oils.
- Frank, F. (8).
- Frank, F. & Marckwald, E. (6) The destructive action of Cu on R. attributed to colloidal Cu sulfide and to insufficient vulc.
- Goodyear, C. (5) See Nitric Acid.
- King, A. H. (1).
- Kogakushi, K. (1) Effect of Cu on tackiness.
- Lascelles-Scott, W. (18) Alkaline cupro ammonium compounds exert a preservative influence on R. (26) CuS harmful to R.
- Marzahn, R. (1) p. 267.
- Morgan, S. (1) See Enzymes.
- Muspratt. (1) Effect of Cu and its salts on R.
- Schwartz, A. (1) Effect of over vulc. and moisture on R. in contact with Cu.
- Seeligman, Torrillon & Falconnet. (1) p. 205. Effect of Cu on vulc. R.
- Snelling, W. O. (1) See Ozone.
- Terry, H. L. (2) Cu, its oxides or salts dissolve O<sub>2</sub> and oxidize R. This action is accelerated by grease. (15) Goods cured in dry heat are less affected by Cu than when cold cured. Insoluble CuS is formed in the first case, soluble salts in the latter. Other metals have little action. No deleterious action of Cr was observed.
- Thomson, W. (3) & (4) Heated Cu oxidizes R.
- Thomson, W. & Lewis, F. (1) R. vulc. with S<sub>2</sub>Cl<sub>2</sub> treated with metals at 140° C. Most injurious in order—Cu, Pt, Pl, Al and Pb. No effect—Mg, Zn, Cd, Co, Ni, Fe, Cr, Sn, As, Sb, Bi, Ag and Au.
- Weber, C. O. (1) & (5) Effect of Cu compounds in textiles on R. See Oxygen. (9) Cu compounds in dyes and action on R. (26) Org. Cu salts

found in the acetone extract of Mozambique R. Such R. cannot be used for cold cures with  $S_2Cl_2$ . In heat cures the Cu changes to the less harmful sulfide. (52) & (60) Effect of Cu on R.

**Copper Dithiocarbamates.**

Molony, S. B. & Nikaido, Y. (1) & (2) See Dithiocarbamates.

**Copper Xanthates.**

Cadwell, S. M. (1) (2) (5) & (6) See Xanthates.

**Cresols.**

**Creosote.** See Latex-Preservatives, Phenols.

Biffen, R. H. (1) See Latex-Coagulation.

Bourn, A. O. (5) Wood creosote imparts desirable properties to compounds containing factis and reclaimed R.

**Cresylic acids.** See Latex-Preservatives.

**Cyanides.**

Dubosc, A. (30) Accelerators.

**Cyanogen.**

Hinrichsen, F. W., Quensell, H. & Kind-scher, E. (1) Cyanogen derivative of R. could not be made.

**Cyclo-octadiene tetrabromide.**

Ostromuiskii, I. (10).

**Dambonite.**  $C_8H_{10}O_4(CH_3)_2 \cdot 3H_2O$ . m.p.  $190^\circ C$ .

Flint, E. R. & Tollens. (1) Isolated Dambonite, Bornesite and a third sugar Matezite.

Girard, A. (1) Dambonite found in Block Gabon R. In Borneo or Madagascar, found no Dambonite but Bornesite (a mono methylether of inosite). It is optically active while Dambonite and Dambos are inactive. Isolated Matezite from Madagascar R.

deJong, A. W. K. (4) See Dimethyl-inositol.

Maquenne. (1) Dambonite identified as dimethyl ether of dambos. Dambos is identical with inactive inosite.

Weber, C. O. (48) Dambonite isolated from Castilloa latex on splitting the glucoside.

**Danialbanes.**

Tschirch, A. & Müller, O. (3) Alpha-danialbane ( $C_{20}H_{32}O$ ) and betadanialbane ( $C_{20}H_{32}O$ ) isolated from Minkindani rubber: "Mozambique balls."

**Depolymerization (Polymerization).** See Ageing, Ageing-Oxidation, Ageing-Tackiness, Light, Viscosity, Vulcanization, Heat.

Alexander, P. (7) See Reclaimed Rubber. (8) The molecular size of R. is variable and affected by physical influences. Regeneration is depolymerization. Heat causes depolymerization.

Asano, K. (1).

Bernstein, G. (3) Depolymerization is affected by heat, light and mechanical working. There is an abrupt change in viscosity at  $60-80^\circ C$ . Complete depolymerization gives the same viscosity figure whether effected by heat, light or mechanical working. (4) See Protein.

Bunschoten, E. (1) m-Dinitrobenzene depolymerizes R. in solution.

Fendler, G. & Kuhn, O. (1) Behavior of raw R. toward solvents is dependent on the degree of depolymerization. Harries, C. (31) p. 8. Effect of boiling solvents on R.

Heurn, F. C. van. (2) R. globules in latex do not have any lower degree of polymerization than those in coagulated R.

King, A. H. (3) Time, temp. and solvents are factors in depolymerization.

Kirchhof, F. (2) Depolymerization must take place before R. will react with S.

Ostromuiskii, I. (10) Depolymerization of R. does not give cyclooctadiene derivatives.

Rossem, A. van. (2) Oxidation of R. is always preceded by depolymerization. (3)  $KMnO_4$  depolymerizes R. in solution. (5) Depolymerization effected by heat, light, mechanical treatment and chemicals. Polymerization increases with temperature and is catalyzed by  $O_2$ . Oxidation only takes place after a lowering of viscosity. R. in a sealed tube at  $130^\circ C$ . goes to a brown syrup on heating. Not observed in  $H_2$ ,  $N_2$  or in vacuo.  $KMnO_4$  and Br also depolymerize R.



- Seidl, E. (4) Vulc. and depolymerization.
- Takeuchi, S. (1) Absolute viscosity used to determine depolymerization of R. during mastication.
- Whitby, G. S. (8) p. 107. Benzoyl peroxide depolymerizes R. in solution.
- Devulcanization.** See Regeneration.
- Dubosc, A. (32) All reactions of vulc. produced by accels. are reversible. Spence used this process in 1915.
- Spence, D. (27) Vulc. R. in Xylene treated with NaOH to react with combined S.
- Dextrosazone.**
- Cadwell, S. M. (3) See Aldehyde-Amines.
- Diacetoneamine.**
- Twiss, D. F. (12) An accel. of the vulc. of R.
- Diacetylpropane.**
- Harries, C. (25) See Rubber Hydrochloride. (26) Formed by decomposing the ozonide prepared from R. regenerated from hydrohalogenated R. with pyridine.
- Lichtenberg, O. (1) From decomposition of ozonides of R.
- Diaminoanthraquinone.**
- Diaminocarbazole.**
- Bayer & Co. (41) See Ageing-Tackiness.
- Di-isoamylamine.** See Di-isoamylamine di-isoamyl-dithiocarbamate and Dithiocarbamates.
- Ostromuiskii, I. (13) An accel. (14) This accel. will vulc. R. at ordinary temp. in presence of metallic oxides. (21) Prevents ageing of R. cured with nitro compounds. (25) See m-Dinitrobenzene.
- Di-isoamylamine - di-isoamyl - dithiocarbamate.** See Di-isoamylamine and Dithiocarbamates.
- Maximoff, A. (1) A strong accel.
- Ostromuiskii, I. (13) (22) An accel. of vulc.
- Diatomite.** See Compounding Ingredients.
- Diazobenzene.**
- Dubosc, A. (30) Mentioned as an accel.
- Dibenzylamine.** See Amines.
- Cadwell, S. M. (5) (6) (7).
- Dibenzyl ether.**
- Bayer & Co. (38) Increases elasticity of vulc. R.
- Di-isobutylamine.** See Di-isobutylamine di-isobutyl-dithiocarbamate and Dithiocarbamates.
- Maximoff, A. (1) A powerful accel.
- Ostromuiskii, I. (22) Used in vulc. of synth. R.
- Di - isobutylamine - di-isobutyl-dithiocarbamate.**
- Maximoff, A. (1) A powerful accel.
- Ostromuiskii, I. (22) Used in vulc. of synth. R.
- Dibutyl-Xanthicdisulfide.**
- Cadwell, S. M. (1) (2) See Xanthates.
- Gibbons, W. A. & Ritter, H. W. (1) R-100, ZnO-10, p-toluidine-4, S-2, Accel.-4.0. Cure 10-30 min./200° F.
- Dichloraniline.**
- deLong, C. R. & Watson, W. N. (1) Equals thiocarbamilide in curing power.
- Dichlorethylene (sym).**
- Fischer, E. (1) See Solvents.
- Diethylamine.** See Aldehyde-Amines, Diethylamine-diethyl-dithiocarbamate and Dithiocarbamates.
- Bayer & Co. (31) An accel. (34) Used with PbO, Sb<sub>2</sub>O<sub>3</sub> and other oxides having available oxygen. (42).
- Ostromuiskii, I. (13) An accel. for synth. R.
- Price, R. B., Brazier, S. A. & Wood, A. S. (1) Preparation from p-nitrosodimethylaniline.
- Diethylamine-diethyl-dithiocarbamate.**
- See Diethylamine and Dithiocarbamates.
- Maximoff, A. (1) A strong accel.
- Molony, S. B. & Nikaido, Y. (1) & (2) Metallic salts as accels. of vulc.
- Schidrowitz, P., Gouvea, J. M. S. & Osborne, F. G. (1) See Dimethylamine-dimethyl-dithiocarbamate.

- Twiss, D. F. (12) (14) Up to 25% of this accel. in a cement without ZnO did not air cure in 27 days.
- Twiss, D. F., Brazier, S. A. & Thomas, F. (1) ZnO is a strong activator. Coefficients, tests and graphs.
- Diethylaniline.**  
Bayer & Co. (15) Used in manufacture of synth. R. (24) See Aniline. (31) Used in R. Compounds to increase elasticity. (32) Used with p-toluidine sulfate. See p-Toluidine. (35) Used with peroxides which liberate O<sub>2</sub> at vulc. temp. See Antimony Oxides. Ostromuiskenskii, I. (25).
- Diethyl-diphenyl-thiuramdisulfide.**  
Cadwell, S. M. (5) (6).
- Diffusion.** See Gases.
- pp-Dihydroxy-diphenylthiourea.**  
Bedford, C. W. & Sebrell, L. B. (1) A fair accel. See p-Amino phenol.
- Dihydroxy-quinoline sulfate.** See Quinoline.
- Di-isopropylamine.** See Dithiocarbamates.  
Bayer & Co. (15) CS<sub>2</sub> and CO<sub>2</sub> derivatives mentioned as accels.  
Ostromuiskenskii, I. (13) An accel. of Vulc.
- Dimethylamine.** See Aldehyde-Amines, Dimethylamine-dimethyl-dithiocarbamate and Dithiocarbamates.  
Bayer & Co. (3) See Ageing-Tackiness. (15) Used in manufacture of synth. R. and left in the product to act as an accel. during vulc. (28) Used to improve ageing of balloon fabrics. (42) See Aniline.  
Gottlob, K. O. (7).  
Hutin, A. (3) Method of preparation.  
King, A. H. (1).
- Dimethylamine-dimethylcarbamate.**  
Twiss, D. F. & Brazier, S. A. (1) An accel. of vulc.
- Dimethylamine - dimethyl - dithiocarbamate.** See Dimethylamine and Dithiocarbamates.  
Anon. (84). (300) This accel. and its homologues are activated by basic oxides especially ZnO.
- Bayer & Co. (6). (13) Ebonite from synth. R. using this accel. (14) Patented as an accel. of vulc.
- Bean, P. L. (1) Disagrees with Tuttle, J. B. (1).
- Bruni, G. & Romani, E. (1).
- Cranor, D. F. (1) Data on curing tests and Sc using smoked sheets and brown crepe. Cures at room temp. See Sulfur-Coefficient.
- Dubosc, A. (30).
- Harrison, M. M. & Morton, H. A. (1) Scorching of high powered accel. on the mills and calenders is prevented by the "two batch" method. Alternate plies of R. containing S in one layer and accel. in the other are built up. The finished composite is gently warmed to allow interpenetration of the chemicals before being vulcanized.
- Hutin, A. (2) Marketed in Germany as "Vulcanisateur." 1% used in hard R. (3) Method of preparation.
- King, A. H. (1).
- Maximoff, A. (1) Lime, MgO and oxides or sulfides of antimony are comparatively inactive with this powerful accel. ZnO is needed. PbO is an aid. 0.85 pts. ZnO are equivalent to 3.5 pts. PbO and should be used with 0.5 pts. accel.
- Molony S. B. (1) The free dithiocarbamic acid is stable and used as an accel. See Dithiocarbamates. (2) Methyl amines from beet sugar residues with CS<sub>2</sub>. R-100, ZnO-50, S-5, Accel.-0.2.
- Morton, H. A. & Harrison, M. M. (1) R. sheeting, etc., usually cured with S<sub>2</sub>Cl<sub>2</sub> is prepared from a mix containing R., S and ZnO. They are formed and dusted with a mixture of starch and this or other accels. and heated for 48 hrs. @ 150° F. Process may be reversed by mixing the accel. into the R. and dusting with S. Painting with solutions may replace dusting.
- Murrill, P. I. (5).
- Schidrowitz, P. (14).
- Schidrowitz, P., Gouvea, J. M. S. & Osborne, F. G. (1) Comparison with the diethyl compound. In absence of ZnO there is little difference. With ZnO the dimethyl derivative is more

active. Tetramethyl thiuramdisulfide is less active than either.

Scott, W. & Bedford, C. W. (1) S in this accel. is not available for vulc. The zinc salt of this accel. will vulcanize without added ZnO.

Simmons, H. E. (1).

Tuttle, J. B. (1) 0.1% retards the cure.

Twiss, D. F. (12). (14).

Twiss, D. F. & Brazier, S. A. (1).

#### **Dimethylaniline.**

Bayer & Co. (5). (13). (15) Used in manufacture of synth. R. and left in the product to act as an accel. during vulc. See Ammonia. (24) Use 10% or more as an elastifier. (31) Use up to 5% to increase elasticity of R. (34) Used with lead and antimony peroxides (which see). (42).

Bedford, C. W. & Sebrell, L. B. (1) Will not air cure a CS<sub>2</sub> cement containing S and ZnO.

Benjamin, E. (1).

Ditmar, R. (62).

Dubosc, A. (40).

Duisberg, C. (1) Used to improve synth. R.

Endres, H. A. (1) Comparison of several accels.

Gottlob, K. O. (7). (8) An accel. and preservative for synth. R.

Hasselt, J. F. B. van. (1) See p-Nitrosodimethylaniline.

King, A. H. (1).

Kratz, G. D., Flower, A. H. & Coolidge, C. (1).

Kratz, G. D., Flower, A. H. & Shapiro, B. J. (1) See Aniline.

de Meeus, E. (1).

Murrill, P. I. (5).

Ostwald, Wa. (1) Used dimethylaniline in 1908 to prevent the ageing or hardening of R.

Ostwald, Wo. & Ostwald, Wa. (1) See Ageing-Tackiness.

Peachey, S. J. (7) A stronger base than p-nitrosodimethylaniline but has less curing power.

Peter, L. (1) Elasticity of synth. R. increased by adding dimethylaniline, petroleum, etc.

Ricard, E. (2).

Rosenbaum, J. L. (1).

Schidrowitz, P. (13) A weak accel. Foul odor.

Twiss, D. F. (7).

#### **Dimethylaniline and CS<sub>2</sub>.**

Ditmar, R. (62) An accel.

King, A. H. (1).

Murrill, P. I. (5).

#### **Dimethyl butadiene Rubber.**

##### **"Normal" Rubber.**

Harries, C. (29) Action of ozone.

#### **Dimethyl-diphenylthiourea.**

Cadwell, S. M. (5) (6).

#### **Dimethyl-diphenyl-thiuramdisulfide.**

Cadwell, S. M. (2) (5) (6). See Xanthates.

#### **Dimethylinositol.**

Jong, A. W. K. de. (4) Obtained from latex of "Melabocai Sumatra." This gave inactive inositol with HI and is probably identical with Girard's "Dambonite."

#### **beta-beta-Dimethyl-d-methyl - trimethyl-eneimine.**

Anon. (84) An accel. of vulc.

Bayer & Co. (13) (14) Used in synth. R. as an accel. of vulc.

Ditmar, R. (62).

Dubosc, A. (30) A very good accel.

Eaton, B. J. (8).

King, A. H. (1).

#### **Dimethyl-alpha-naphthylamine.**

Martin, R. B. (1) See Ageing.

#### **Dimethyl-succinic-aldehyde.**

Bayer & Co. (17) (18) See Ozone.

#### **Dimethyl-thiuramdisulfide.**

Romani, E. (1) Low curing power.

Twiss, D. F. (14).

Twiss, D. F., Brazier, S. A. & Thomas, F. (1) Less active than the tetramethyl derivative.

Williams, I. & Beaver, D. J. (1) An accel. of vulc.

#### **Dimethyl-o-toluidine.**

Bayer & Co. (15). (24) Used in manufacture of synth. R. and left in the product to act as an accel. during vulc.

**Dimethyl-p-toluidine.**

Bayer & Co. (24) Use 10% or more as an elastifier. (31) Use up to 5% to increase elasticity of R.

**Dinitroanthraquinone.**

Dannerth, F. (1).

Gibbons, W. A. (1) Will vulc. R. without S either with or without PbO. R-100, Dinitroanthraquinone-30, cure 2 hrs./306° F. R-100, Dinitroanthraquinone-5, PbO-10, cure 1 hr./286° F.

**m-Dinitrobenzene.**

leBlanc, M. & Kröger, M. (1) See Viscosity.

Dubosc, A. (35) Dinitrobenzene will not vulc. R.

Ostromuiskii, I. (19) The relative value of metallic oxides as aids in vulc. of R. by nitro compounds given as PbO, ZnO, CaO, MgO, BaO. Org. accels. retard vulc. by nitro compounds. Formulae, cures and tests are tabulated. (25) Nitrobenzene, dinitrobenzene, trinitrobenzene, nitrotoluenes, tri- and tetra-nitronaphthalenes, picric acid, picramic acid, picryl chloride, aurotin, artificial musk, nitrocyclohexane and other nitro compounds patented as vulcanizing agents without S in presence of metallic oxides or with a small amount of S. Process is assisted by sodium alcoholate, naphthylamine, pyridine, piperidine, di-isoamylamine or antimony sulfides.

Porritt, B. D. (2) Inactive in absence of metallic oxides.

Rossem, A. van. (11) Blooms out on the cured R. m-Nitraniline identified in the bloom. Org. accels. retard its curing action. Tables, formulae, cures and tests.

Somerville, A. A. & Rentschler, M. J. (1) R. is vulc. with dinitrobenzene and PbO in contact with metals to avoid tarnishing.

Stevens, H. P. (8) R-100, Dinitrobenzene-2 and a blank gave no trace of cure when wrapped and cured in steam 3 hrs. 135° C. (14) Mono-, di- and trinitrobenzene and benzoyl peroxide tried as vulc. agents. Trinitrobenzene gave no cure without PbO. With PbO or MgO both di- and trinitrobenzene cured. Same amount of

benzoyl peroxide required for vulc. as with S but vulc. takes place in shorter time.

**Dinitro-dihydrocuminic acid.**

Ditmar, R. (4) Formed by fuming HNO<sub>3</sub> on R. See Nitric Acid.

**Dinitro-dimethyl-benzoic acid.**

Parepa, M. C. D. (1) Conc. HNO<sub>3</sub> on isoprene gives oxalic acid and CO<sub>2</sub>, on caoutchine it gives dinitro-dimethyl-benzoic acid.

**Dinitroso-pentamethylenetetramine.**

Dubosc, A. (40) An accel. (48) Used with 1 mol CS<sub>2</sub> for vulc. of R.

**Dinitrosophenol.**

Bayles, E. A. (1) An accel. in R. cable covers. Retardants such as phenylhydrazine, methylene blue or glucose are used with it.

**Dioxyanthraquinone.****Dioxynaphthalene.**

Bayer & Co. (41) See Ageing-Tackiness.

**Diphenylamine.** See Aldehyde-Amines.

Bayer & Co. (31) Up to 10% used to increase elasticity of R.

Gottlob, K. O. (8) An elastifier for synth. R.

Hasselt, J. F. B. van. (1) See p-Nitrosodimethylaniline.

Twiss, D. F. (7) Used with metallic sodium as an accel.

**Diphenylguanidine.** (D. P. G.).

Anon. (142) "Speed-X." Consists of 60% D. P. G. and 40% ZnO.

Bedford, C. W. & Sebrell, L. B. (2) Reactions of.

Dovan Chem. Co. (1) License for sale of D. P. G. under Hofmann & Gottlob, U. S. P. 1,149,580. Grasselli Chem. Co. See Bayer & Co. (19).

(2) X. L. O. Commercial accel. consisting of 1/3 magnesium oxide and 2/3 D. P. G.

Kratz, G. D., Flower, A. H. & Coolidge, C. (1) A more powerful accel. than triphenylguanidine but equal to monophenylguanidine wt. for wt. See Aniline.

Scott, W. (2) Chemistry of D. P. G. and disubstituted guanidines. Di-o-

tolylguanidine is most active, di-*p*-tolylguanidine is next and then D. P. G. ZnO has a favorable effect on these accels.

Scott, W. & Bedford, C. W. (1).

Weber, L. E. (9) Non-poisonous. Does not scorch or discolor. High cost is balanced by increased activity. Not over 3/4% should be used. See Triphenylguanidine.

Weiss, M. L. (1) Accel. of vulc. with a disubstituted guanidine, such as D. P. G. (2) Process of manufacture.

**Diphenylthiourea.** See Thiocarbanilide.

**Diphenylthiuramdisulfide.**

Maximoff, A. (1) An accel.

**Diphenyltoluylenediamine.**

Bayer & Co. (41) See Ageing-Tackiness.

**Diphenylurea.** See Carbanilide.

Dubosc, A. (40) An accel. of vulc.

**Dipiperidyl.**

Gottlob, K. O. (8) A fair accelerator.

**Distillation of Rubber.**

Achard, F. (1) Dry distillation products of R. are carbonic acid, hydrocarbons, ammoniacal water and empreumatic oils.

Adriani, A. (1) Dry distillation of R. (1850). See Gutta Percha.

Anon. (168) Kautschin, the distillate from R. as a R. solvent.

Aiken, A. (1) Dry distillation product of R. used as a paint for steel to prevent oxidation of the latter.

Bamber, M. K. (6) Distillation of R. to produce solvents and a residue termed "liquid R."

Barnard, W. H. (1) Distilled R. in iron retort by heating at 600° F. Distillate dissolved R., resins, fatty bodies and could be used as an illuminant. Odor removed by treatment with chlorine or nitro-muriatic acid.

Beale & Enderby. (1) Oil from distillation of R., a solvent for R. and copal. Used to make a varnish.

Berniard, R. (1) Berniard was the first to distill R. and collect the oily product (1781).

Bouchardat, A. (1) Isolated Butylene, b.p. 10° C., and caoutchene b.p. 14.5° C. at 752 mm., from dry distillation

products of R. Caoutchene is insol. in H<sub>2</sub>O, soluble in absolute alcohol and ether. He also obtained Eupion and Hevene, b.p. 315° C. Liquid at ordinary temp. Absorbs chlorine easily, giving off HCl and is converted into a black resin. (2) Purified turpentine resembles the oil obtained from R. by dry distillation.

Bronde, W. T. (1) Résumé of early work.

Cayla, V. (6) Résumé of work on distillation of R. and constitution of natural or synth. R.

Chevallier. (1) Confirmed the solvent properties for R. of dry distillation product of R. He called it Caoutchoucine, yield 88.92%.

Clouth, F. (1) p. 107.

Dalton, J. (1) Physical and chemical properties of R. distillate (1834).

Ditmar, R. (6) Different fractions from distillate of R. behave differently towards HNO<sub>3</sub>. Below b.p. of 300° C. resins are obtained, above 300° C. a dinitro acid. On dry distillation R. molecule splits into aliphatic terpenes of which isoprene is the lowest member. These compounds polymerize to dipentene and polyterpenes. Caoutchene is a cyclic terpene, which should be called dipentene. Caoutchene should not be confused with caoutchene isolated by Bouchardat, A. (50) p. 17. Discussion of literature.

Dubosc, A. (37) Production of acetylene by distillation of R. was not mentioned by Himly, Williams, A. Bouchardat or G. Bouchardat, Weber, or Fischer & Harries. In distillation of uncured R. the gases evolved are CO, ethylene and methane. Study of distillation of vulc. R. (38) Dry distillate of tire beads contained acetic acid, benzene, toluene, xylenes, ethyl benzene, dipentene and no isoprene or Hevene. The gases were H<sub>2</sub>S and acetylene. Decomposition started to be vigorous between 75° to 145° C. and was complete at 245° C.

Dubosc, A. & Luttringer, A. (1) Résumé of researches.

Enderby. (1) First patent on distillation of R. Fischer, E. and Harries, C. (1) Distilling R. in vacuo, a product boiling 180°-300° C. was ob-

- tained. Only a little isoprené and dipentene.
- Fourcroy, A. F. (1) On dry distillation of R.
- Fonrobert, E. & Harries, C. (1) Discussion of literature.
- Gottlob, K. O. (6) p. 10. Discussion of literature. R. softens at 120° C. and changes into a thick brown syrup at higher temp. Almost quantitative yield of Kautschukin, boiling from 18° to 300° C. is obtained by dry distillation of R. Lower fractions have properties of aliphatic terpenes, higher fractions those of aromatic terpenes.
- Gregory, W. (1) Separated distillate boiling at 35° C. and after treating with H<sub>2</sub>SO<sub>4</sub> obtained a product boiling at 226° C. Analysis of R. distillate.
- Harries, C. (2) Isolated di-isoprene from R. distillate which is similar or identical with myrcene. (16) (24) R. cannot be distilled in vacuo without decomp. (31) p. 9.
- Heinzerling, C. (1) p. 30.
- Himly, F. C. (1) Isolated dipentene. Described the chloride and hydrochloride of the oil obtained by dry distillation of R. "Kautchin" a distillate of R. b.p. 171.5° C. Eupion b.p. 33°-44° C. Caoutchecine.
- Ipatiew, W. & Wittorf, N. (1) Obtained isoprene, on dry distillation of R.
- Klaproth, M. H. & Wolff. (1) Distillation of R. gives CO<sub>2</sub> and NH<sub>3</sub>.
- Lebeuvre, C. (1) Distillation of scrap R. to produce an oil similar to turpentine.
- Leonhardi, J. G. (1) Achard's work on distillation of R.
- Liebig, J. (1) obtained results similar to those by Gregory, W. (1).
- Liebig, J., Poggendorff, J. C. & Wöhler, Fr. (1) p. 64-71. Résumé of A. Bouchardat and F. C. Himly's work.
- Louguinine. (1) Dry distillation of R. (1888).
- Luff, B. D. W. (1) Review of early work on dry distillation of R.
- MacLagan, D. (1) Dry distillation of gutta percha.
- Perkin, F. M. (1) Review of work on distillation of R.
- Pictet, A. (1) Distilling R. under reduced pressure gave same products as at ordinary pressure.
- Ramsay, Chick & Collingridge. (1) Distillation of gutta percha.
- Schidrowitz, P. (6) p. 144. Discussion of literature.
- Schmidt, E. A. (1) See Gutta Percha.
- Schuller, A. (1) On slight warming in vacuo two volatile constituents come over. The more volatile portion has odor of R. Residue has little odor and is tacky but does not appear to be decomposed.
- Seeligmann, Torrilhon & Falconnet. (1) p. 125.
- Staudinger, C. & Fritsch, H. (1) See Hydrogen.
- Traun, H. O. (1) p. 43. Dry distillation products of R.
- Trommsdorf, J. B. (2) Prepared an oil from R. by dry distillation, yield 80-84%.
- Wallach, O. (1) Isolated a polyterpene boiling above 300° C.
- Weber, C. O. (7) The slower the dry distillation or lower the temp. the smaller is the yield of isoprene and citrene. (61).
- Wiesner, J. (7) p. 387. Dry distillation of R. gives CO<sub>2</sub>, CO, Rubber oil, Kautschucin, Himly's Kautschin C<sub>20</sub>H<sub>30</sub>, Heveene, water containing ammonia, sulfur and chlorine compounds and a residue of carbon.
- Williams, G. (1) Isolated isoprene and caoutchine b.p. 171.5° C., C<sub>20</sub>H<sub>30</sub>, in distillate of R. See Caoutchecine.
- Disulfides.** See Tetramethylthiuram-disulfide and monosulfide, Thiuram-disulfides.
- Bedford, C. W. & Sebrell, L. B. (1) (2) See Mercaptobenzothiazole.
- Bruni, G. & Romani, E. (1) See Mercaptobenzothiazole.
- Cadwell, S. M. (1) Disulfides of xanthic acids. See Xanthates. (5) & (6) Disulfides of mono- and dithioacids, of xanthic, thiol and other sulfur acids as accels. with or without the aid of an organic amine. (7) Thiol benzoic-anhydride, benzoyl-butyl-xanthogenate and thiuram monosulfides as accels. of vulc.
- Kimishima, T. (1) See Thioaniline and Vulcanization-Theories.

Romani, E. (3) (4) Disulfides of dithioacids and nitrogen sulfides are capable of vulc. R. without free S.

#### **Dithio-acids.**

##### **Monothio-acids.**

Bruni, G. (5) Preparation of dithioacids by action of aldehydes on ammonium polysulfides. Disulfides and metallic salts are mentioned. (6) Zinc salts of these acids are ultra accelerators. Zinc dithiobenzoic- and zinc dithiopyromucic acid. Such acids are prepared by action of ammonium polysulfide on benzaldehyde, anisic aldehyde, salicylic aldehyde, citral, citronellal or etc. The lead salts or the disulfides are also accels. Dithiobenzoyledisulfide will vulc. R. without S.

Cadwell, S. M. (5) K, Pb, Zn, Cd, Hg, Cu, etc., salts of mono and dithioacids as accels. of vulc. with or without the assistance of amines. See Amines and Xanthates.

Romani, E. (3) Dithiobenzoic, dithiopyromucic, dithiosalicylic, dithioanisic, dithiovanillic and dithiopiperonic acids, their zinc salts and disulfides. Methods of preparation and use as accels. of the vulc. of R. (4) Lead salts of dithioacids are less active than zinc salts. Monothioacids, their zinc salts and disulfides are inactive as accels.

#### **Dithioaniline.**

Kimishima, T. (1) See Thioaniline.

#### **Dithiobenzoyledisulfide.**

Cadwell, S. M. (1) See Xanthates.  
Bruni, G. (7) See Dithioacids.

**Dithiocarbamates.** See Aksel, Diethylamine-diethyl-dithiocarbamate, Diisoamylamine - di - isoamyl - dithiocarbamate, Dimethylamine-dimethyl dithiocarbamate, Phenyl-dithiocarbamic acid, Piperidine-pentamethylene-dithiocarbamate.

Anon. (93) "Aksel." A dithiocarbamate accel. Works well with PbO, lime and MgO but not with antimony sulfides.

Bedford, C. W. & Gray, H. (1) Metallic dithiocarbamates are true accels. Metallic oxides are necessary to

prevent decomp. of metallic salt by  $H_2S$ .  $H_2S$  changes thiourams to dithiocarbamates and dithiocarbamates change to metallic salts.  $NH_3$  increases curing power of thiuramdisulfides and zinc dithiocarbamates.

Bedford, C. W. & Sebrell, L. B. (1) Zinc salts of phenyl-dithiocarbamic acid will vulc. a R-S-ZnO mix at ordinary temperature. See p-Aminophenol. (2) Mechanism of vulc. and chemical reactions.

Bedford, C. W. & Scott, W. (1).

Bruni, G. (1) Mg, Zn, Cd, Hg, U, Al, Cr and Sb salts of mono- and dialkylated dithiocarbamates as accels. of vulc. Zinc pentamethylene dithiocarbamate as an accel. (3) R-100, S-8, ZnO-20, Aniline-6. Expose this mix to vapors of  $CS_2$  and vulc. takes place without the application of heat. (6).

Bruni, G. & Romani, E. (1).

Cadwell, S. M. (5) (6) Patents.

Luttringer, A. (1) Abstract of Bruni (3).

Maximoff, A. (1) Ammonium dithiocarbamates are unstable and have lower curing power than dithiocarbamates of secondary aliphatic amines. See Benzyl-ethylamine. (2) Vulc. of mixtures of leather and R. at temperatures so low that the leather will not scorch, by use of dithiocarbamate accels.

Molony, S. B. (1) Alkylated dithiocarbamic acids made by exposure of the ammonium salts to air or by their oxidation with  $H_2O_2$  are more stable and valuable as accels. (2) Accels. by action of  $CS_2$  on the amines obtained from beet sugar residues.

Molony, S. B. & Nikaido, Y. (1) (2) Metallic salts and esters of mono and diarylated or alkylated dithiocarbamates as accels. of vulc. Methyl ester of phenyl-dithiocarbamic acid, methyl ester of dimethyl-dithiocarbamic acid, Zn, Mn, Mo, Sb, Sn, Cu, Fe, Cr, As and Hg salts of methyl, ethyl, propyl or other alkyl dithiocarbamic acids.

Murrill, P. I. (4) (5) (6) Oxidation of metallic salts of dithiocarbamic acids.

Ostromuiskii, I. (31) See Hexa and Piperidine - pentamethylene-dithiocarbamate.

- Twiss, D. F. (14) Zinc dithiocarbamates need ZnO to bring out their full curing power. Dithiocarbamates from primary amines are weaker accels. than those from secondary amines.
- Twiss, D. F., Brazier, S. A. & Thomas, F. (1) Zinc dithiocarbamates are almost inactive in absence of ZnO.
- Dithiocarbonates.** See Trithiocarbonates and Xanthates.
- o-Ditolylthiourea.**
- Scott, W. (1) Exceptional activity at low temp. is claimed for this accel. in the presence of ZnO.
- Twiss, D. F. (12) Mentioned as Thio-carbo-o-toluidide.
- p-Ditolylthiourea.** See Thiocarbo-p-Toluidide.
- Dixanthogens.**
- Bruni, G. & Romani, E. (1) See Xanthates.
- Dixyl Ether.**
- Bayer & Co. (38) Increases elasticity of vulc. R.
- "Duroprene."** See Chlorine (Chlorinated Rubber).
- Dyes.**
- Anon. (225) Cu salts in cotton dyed with S dyes causes deterioration of R. (245) R. articles dipped into a solution of R. containing a pigment and then vulc. with  $S_2Cl_2$ .
- Bayer & Co. (10) Dyes suitable for R. mixes. Thio indigo Scarlet R., Pyranthrene, Indanthrene blue, Thio indigo Red B, Indanthrene Yellow, Helio yellow Solid 8 G. L. extra, Helio red solid, Helio Bordeaux solid B. L., Orange ceres, etc. (12) Azo dyes such as Helio echtrot do not lose their color when used in ebonite cured at 170° C.
- Bedford, C. W. & Sebrell, L. B. (1) Many sulfur dyes are inactive as accels. of vulc. after removal of free alkali.
- Camille, A. (1) (2) (5) Coloring R. (3) Use of indigo in R. (4) Mineral colors for R. (6) Aniline black, eosines and aniline dyes in R. (8) Use of mordants in R.
- Dannerth, F. (3) Coal tar industry supplies aniline and thiocarbanilide for use as accels. A large field is open for use of coal tar dyes as substitutes for mineral coloring pigments.
- Davenport, B. F. (1) See Poisoning.
- Ditmar, R. (54) Vat dyes are stable during vulc., also those which have a high mol. wt. and show a tendency to form colloidal solutions. (57) Tests on 100 dyes for R. goods. (58) Mixing R. with S and organic vat dyes prior to vulc.
- Dubosc, A. (40) Sulfur dyes as accels. of vulc. (60) Reduction products of p-nitraniline red are accels. p-phenylenediamine and aminonaphthol are formed.
- Ford, A. (1) R. articles dipped in aqueous solutions of aniline dyes at 150° F. Solvents such as ether,  $C_6H_6$  or  $CH_3OH$  may also be used.
- Gaisman, L. & Rosenbaum, J. L. (1) Triphenylmethane dye bases as accels. of vulc.
- Gastinger, H. (1) Description of German enameling processes. Formulas of various colored enamels.
- Gottlob, K. O. (5) Azo dyes such as helio fast yellow 8 G. L. mixed with R. prior to vulc. with S.
- Harrison, M. M. (1) R. balloons after vulc. are dipped into aniline coloring matter dissolved in a R. solvent.
- Lascelles-Scott, W. (24) Coloring of R. and characteristics of an ideal pigment.
- Leheup, C. E. (1) Coloring R.
- Leightfoot. (1) Coloring R. articles by dipping in aniline red or violet, also Murexide.
- Lewis, E. W. (1) Different methods of coloring R.
- Markfeldt, O. (1) Dye must withstand temp. of 140° C. and should not be acted upon by S at that temp. Pb, Fe, Sn, Hg and Cu cannot be used. Aniline dyestuffs have not been successful.
- deMeus, E. (1) Victoria green and blue bases and triphenylmethane dye bases as accels. of vulc.



- Norris, W. (1) Coloring R.  
 Ostromuiskii, I. (16). (28) R., an organic dye, S, an amine and a metallic oxide are mixed and vulc. below 212° F. (31) Dithiocarbamates trinitrobenzene or benzoyl peroxide vulc. R. at a sufficiently low temp. to prevent the loss of color of organic dyes.  
 Paulet, F. (1) Use of an iodide for coloring R.  
 Repony, D. (2) Chlorophyll is the only vegetable color that can replace mineral colors in R. No change in color for 30 min./290° F.  
 Rhyn, H. C. van. (1) Coloring of R. and printing on surface of R.  
 Seidl, E. (3) Coloring vulc. R. with dyes.  
 Somerville, A. A. (1) R. compounded with light sensitive material, the mass is formed to shape, exposed to light and vulcanized.  
 Spence, D. (24) R. treated with aqueous solution of an amine. The absorbed amine is diazotized and combined with a dye component so that an azo dye is obtained combined with or fixed on the R.  
 Turpin, E. (2) R. colored with eosin and fluorescein lakes prepared from zinc chromate or oxide and K eosinate.  
 Weber, C. O. (27) Use of colored pigments in R. (30) Use of color lakes in R.
- Ebonite.**  
**Hard Rubber.** See Vulcacite P.  
 Anon. (218) Properties and preparation of ebonite. (224) Historical regarding the hard rubber industry.  
 Bayer & Co. (5) See Piperidyl Urea.  
 Blossom, T. M. (1) Mentions Nelson Goodyear (1).  
 Bolas, T. (5) Ebonite warmed to 100° C. will bend and can be remolded. Melts at 230° C. with permanent change. Melted ebonite used as binder in emery wheels. Such emery wheels introduced by Delapauque prior to 1880. S was added and the molded wheel was revulcanized by baking at 140° C.  
 Clapp Rubber Co. (1) Solutions of ebonite are obtained by use of a solvent consisting of terpenes which have been heated with oxalic acid.  
 Dieffenbach, G. (1) Dental ebonite by heating R. with aluminium sulfite.  
 Duisberg, C. (1) & (2) See Piperidine.  
 Frank, F. & Marckwald, E. (8) Para R. said to be incapable of forming hard R.  
 Glancy, W. E. (1) Influence of certain compounding ingredients in hard R. Influence of resin, lime, MgO, S and reclaim.  
 Goodyear, Nelson. (1) First patent and discovery of ebonite. Used MgO and lime, their carbonates or sulfates. Also shellac, rosin, oxides of Pb or Zn, etc.  
 Henriques, R. (1) Hard R. dissolves in paraffin at temperatures over 300° C. H<sub>2</sub>S is evolved.  
 Hübener, G. (1) Analysis by tetrabromide method.  
 Immisch, O. C. (1) Ebonite becomes soft at 400 to 440° F. and may be remolded.  
 Mayall, T. J. (1) See Antimony Sulfides.  
 Mayer, A. M. (1) See Polysulfides.  
 Paterson, C. C., Rayner, E. H. & Kinnear, A. (1) Exposure of ebonite to light reduces surface insulation due to formation of acid on the surface.  
 Wildermann, M. (1) Ebonite resistant to caustic and chlorine.
- Egg albumin.** See Protein.
- Enzymes.**  
**Bacteria.**  
**Chromogenic organisms.**  
**Micro organisms.**  
**Mold.**  
**Oxidases.**  
**Peroxidases.**  
**Spotting of rubber.**  
 Anon. (81) HCHO, quick drying and use of NaHSO<sub>3</sub>, prevent infection of the R. and formation of colored spots. (242) Red spots formed by bacterium prodigiousus on drying are caused by impurities in coagulating bath and starch constituents of R. (259) Spotting and discoloration of Plantation R.  
 Arens, P. (4) Cause of red spots on fresh R. (6) See Ageing-Tackiness.

- (7) Thorough drying of R. prevents mold formation. Moldy R. may be treated with quinosol solution.
- Austriacus. (1) See Ageing-Tackiness.
- (2) Mold on plantation R.
- Bamber, M. K. (3) Discoloration of R. may be prevented by destroying the enzyme in the R. or latex by heat.
- Bancroft, K. (1) Spots on plantation R. due to micro-organisms. Use of formol and smoke as preventatives.
- Beadle, C. & Stevens, H. P. (15) Darkening of crude R. is due to presence of an oxidase. Its action is inhibited by  $\text{NaHSO}_3$  without injurious effect on the vulcanizing properties of the R.
- Berry, A. E. & Boake, A. (1) Darkening of R. inhibited by  $\text{SO}_2$ .
- Bertrand, G. (1) & (2) See Ageing-Oxidation and Ageing-Tackiness.
- Brooks, B. J. (1) The occurrence of red patches on crepe R.
- Cayla, V. (1) Oxidases in latices of 18 different plants. All R. latices when fresh contain either an oxidase, a peroxidase or a catalase, which are concerned in the coloration and possibly spontaneous coagulation of R. No oxygenase found in latex preserved with ammonia. (2) Effect of enzymes on coagulation of R. Peroxidase present in latex.
- Davidson, S. C. (9).
- Eaton, B. J. (3) Addition of amidol, hydroquinone and p-phenylene diamine causes rapid darkening in coagulum obtained by acetic acid, which may be prevented by  $\text{NaHSO}_3$  or by excluding air. (22) Chromogenic organisms develop on dry crude R. which later becomes damp. This organism may destroy the nitrogenous accelerator present in the R. (32) Pink spots do not affect the quality of the R.
- Frank, F. & Marckwald, E. (3) See Ageing-Tackiness.
- Gardner, H. C. T. (2) See Ageing-Tackiness.
- Gorter, K. (10) Enzymes do not produce tackiness.
- Hartjens, J. C. (2) Spots on sheet R.
- Kaye, F. (1) Color of R. not due to enzymes but to oxidation of proteins.
- Kemp, J. S. (1) R. suffers no physical injury due to fungus growth. Insufficient drying and smoking, unstandardized latex, use of chemicals that cause molds, are the chief causes for formation of mold.
- Lecompte, H. (1) First described presence of an oxygenase in fresh Hevea, Castilloa and Manihot latices.
- Morgan, S. (1) p. 161. Tackiness not directly due to bacteria, enzymes or putrefaction. Mold is more pronounced in R. from rich latex. Creosote and formalin do not prevent mold.  $\text{KMnO}_4$  prevents mold but a trace is injurious to R.  $\text{CuSO}_4$  was tried with disastrous results. p. 169. Spots are due to bacteria and fungus, they do not occur in smoked sheet. Netherlands Government Institute. (5) "Spots" have no effect on mechanical properties of the R. They develop at the expense of the secondary compounds and not of the R.
- O'Brien, T. E. H. (1) See Rustiness. Mold is lessened by soaking sheets of R. in running water.
- Pearson, H. C. (1) p. 52, Cause of color in R. Résumé.
- Petsch, T. (2) Bacteria or yeasts cause "spotting" of R. biscuits.
- Rossem, A. van. (3) Presence of mold does not indicate poor quality.
- Scott, J. (2) Vulc. R. exposed to moist air may develop a micro-fungus. The R. wrinkles in a peculiar manner and may become very weak.
- Sharples, A. (1) Conditions which favor the growth of fungi and methods of prevention of spotting. Dilution of latex or excess of coagulant favor "spotting."  $\text{HCHO}$  and  $\text{NaHSO}_3$  are preventatives.
- Schidrowitz, P. & Goldsbrough, H. A. (2) Excess of acetic acid in coag. checks mold in the R.
- Söhngen, N. L. & Fol, J. G. (1) In presence of moisture bacteria and mold fungi develop at expense of proteins, sugars and resins, giving colored spots on R. Properties of R. are unaffected. Found 2 species of Actinomyces capable of assimilating the R. molecule.
- Spence, D. (7) True oxidase in *Funtumia elastica* and *Hevea Brasiliensis* latices. (8) Enzymes give color

- to R. (9) Theory of function of oxidase enzymes in R. proteins which cause darkening of the R. Extracted a peroxidase from Para R. (15) Hevea Brasiliensis and Funtumia elastica latices digested with trypsin. Over one-half of protein of the latex could be removed without coagulation.
- Spoon, W. (1) See Quinosol.
- Stevens, H. P. (36) Discussion of the literature. Cause of mold and darkening of smoked sheet. Use of quinosol to prevent "spots." (46) Moldy portions of a smoked sheet cure more slowly than the clean portions. Vulcanizing properties of smoked sheet unaffected by soaking in water or preservative containing HCHO. (75) Moisture and mold increase the difference in rate of cure of Plantation R. in a PbO stock.
- Thame, J. (1) Drying R. in a current of air mixed with vapors of phenol or cresol to prevent mold in the raw R.
- Vernet, G. (2) Action of oxidases. (4) Found a peroxidase in tissues outside of the latex vessels.
- de Vries, O. (19) Soaking in water 5-20 hrs. effectively prevents mold. (24) p. 27 & 157. A coagulating enzyme has not been isolated in latex. Arguments in favor of an enzyme action in coagulation. p. 371. Mold and its prevention.
- Weber, C. O. (48) Darkening of R. from *Castilloa elastica* latex due to oxidizing enzyme in the latex.
- Whitby, G. S. (1) A peroxidase but no oxidase found in Hevea latex. See Latex-Coagulation. (8) p. 56. Discoloration of R. due to oxidase activity has no influence on vulcanizing properties of the R. p. 57. Phenols accelerate activity of the oxidase, thus explaining why Hevea R., fine hard Para and smoked sheet discolor due to phenolic bodies in the smoke.  $\text{CaCl}_2$  and  $\text{AgNO}_3$  also accelerate oxidase activity in latex. p. 160. Cause and prevention of the "spotting" of R. Spotting fungi may diminish rate of cure by destroying or neutralizing the natural accel. formed by protein decomposition.
- Wildeman, E. de. (1) Colored spots in plantation R. are caused by chromogenic bacteria.
- Ether(s).** See Latex-Coagulants and Solvents.
- Bayer & Co. (38) Aryl or alkyl ethers increase the elasticity of R.
- Ethylamine.** See Aldehyde-Amines and Dithiocarbamates.
- Cadwell, S. M. (1) See Xanthates.
- Dubosc, A. (54) Dissolves in cold furfural and the saturated solution is used as accelerator in dry heat vulc.
- Maximoff, A. (1)  $\text{CS}_2$  on ethylamine. See Dithiocarbamates.
- Ostromuiskenskii, I. (13) An accel.
- Ethylamine-diethyldithiocarbamate.** See Dithiocarbamates and Ethylamine.
- Ethylamine-ethyldithiocarbamate.** See Dithiocarbamates and Ethylamine.
- Ethyl Aniline.**
- Martin, R. B. (1) See Ageing.
- Ethylene.**
- Himley, F. C. (1) Ethylene is one of the dry distillation products of R.
- Ethyl esters of thiocarbamic acids.**
- Cadwell, S. M. (5) & (6).
- Ethylidene Aniline.**
- Cadwell, S. M. (3) The reaction product of acetaldehyde and aniline as an accel. Method of manufacture. See Aldehyde-Amines.
- Ethyl Iodide.**
- Lascelles-Scott, W. (4) See Sulfur Chloride.
- Ethyl oxyester of potassium thiolcarbonate.**
- Cadwell, S. M. (5) & (6) An accel.
- Ethylphenylthiourea.**
- Cadwell, S. M. (5) & (6) An accel.
- Ethyl Xanthates.**
- Cadwell, S. M. (1) (4) (5) & (6) See Xanthates.
- Eucalyptus Oil.**
- Camille, A. (13) Dissolves R.
- Lascelles-Scott, W. (6) Dissolves R. (7) Accelerates the solution of R. in

- benzene. Camphor and menthol do not have this action. Benzene-92 and eucalyptus oil-8 dissolves all good rubbers.
- Eupione.** b.p. 33°-44° C.  
Bouchardat, A. (1) See Distillation of rubber.  
Himly, F. C. (1) See Distillation of rubber.
- Eureka compound.** See Lead Hyposulfite.
- Factis.** Vulcanized oils.  
Anon. (102) Factis in R. compound-ing. Retards bloom. (116) Factis in R. mixings. (246) White substitute less deleterious to elasticity of the product than brown substitute. MgO used to neutralize acidity.  
Bayer & Co. (37) Accels. for preparing factis. (38) S in-oil in presence of an accel. such as Vulcacite P gives factis of any desired hardness.  
Burghardt, C. A. (2) See Ageing.  
Ditmar, R. (54) Factis and dyes are incompatible in R. (59) Acetone extract and free S in factis. (62) Brown factis retards vulc. of R. See Iron Oxide.  
Ditmar, R. & Dinglinger, O. (1) See Ageing-Oxidation.  
Donath, E. (2) Factis protects R. from oxidation.  
Halen, S. (1) Patent review on R. substitutes.  
Henriques, R. (2) White and brown substitutes.  
Hornung, E. & Hansel, S. (1) See Ageing-Tackiness.  
Schulze, E. (3) See Sulfur.  
Seidl, E. (2) Manufacture of white and brown factis.  
Stamford Rubber Supply Co. (1) Factis in R. goods.  
Thomson, W. & Lewis, F. (1) See Metallic Salts.  
Vaubel, W. (2) Properties of factis.  
Warren, T. T. P. B. (1) Heating oils and S to produce a compound for admixing with R.
- Faradayin.** Same as Caoutchukin (rubber oil).
- Ferric Dithiocarbamates.**  
Molony, S. B. & Nikaido, Y. (1) (2) See Dithiocarbamates.
- Ferric Oxide.** See Iron Oxide.
- Ferrocyanide.** See Sodium Ferrocyanide.
- Fish scales.**  
Heyl, G. E. (1) R. vulc. with finely ground fish scales.
- Fluavil.** See Alban & Gutta Percha.  
Allen. (1) Abstracts of literature.  
Anon. (196).  
Berry, W. C. (1).  
Bolas, T. (6).  
Bornträger, H. (1) b. p. 105° C.  
Ditmar, R. (12) & (45).  
Oesterle, O. (1) Analysis. (2) Causes gutta percha to become hard and brittle.  
Payen, M. (1) A non-crystalline constituent of gutta percha.  
Ramsay, Chick & Collingridge. (1) Properties of, analysis, etc.  
Razmann, R. (1) Chemically inactive.  
Tschirch, A. & Müller, O. (1), (2) & (3) Fluavil in gutta percha.
- Fluorine.**  
Seeligman, Torrillon & Falconnet. (1) p. 163. Energetic action on R.
- Fluosilicic Acid.** See Latex-Coagulants-Hydrofluosilicic Acid.
- Formaldehyde.** See Latex-Preservatives.  
Anon. (261). (262). (266a) See Variability.  
Campbell, L. E. (4) Add. of HCHO to latex retards the rate of vulc. of smoked sheet.  
Eaton, B. J. & Grantham, J. (5) and Eaton, B. J., Grantham, J. & Day, F. W. F. (1) Soaking rolled crepe in HCHO retards maturation and rate of vulc.  
Gorter, K. (3) Found HCHO in Smoked sheet.  
Schidrowitz, P. & Kaye, F. (2) HCHO on Funtumia Elastica.  
deVries, O. (15) Soaking R. in HCHO retards rate of vulc.
- Formaldehyde-aniline.** See Methylene-aniline.
- Formanilide.** See Methylene aniline.  
Bayer & Co. (31) 5% in R. as an accel.  
Eaton, B. J. (9).  
Ricard, E. (2).

**Formic Acid.**

Allen. (1) p. 156. By action of nitric acid on gutta percha.

Harries, C. (29) Formed by ozonizing rubber.

**Formimine.**

Anon. (84).

Dubosc, A. (40).

**Formoguanidine.**

Dubosc, A. (40).

**Furfural Derivatives.****Furfuraldehyde. Pyromucic aldehyde.****Furfur-amide. "Vulcazol."**

Dubosc, A. (7), (40) & (54) An active, non-poisonous accel. Compounding data.

Mains, G. H. & Phillips, M. (1) Condensation of furfural with amines.

Miner, C. S., Trickey, J. P. & Brownlee, H. J. (1) Uses of furfural. Bibliography.

Murrill, P. I. (5).

Ricard, E. (1) Patent on furfural derivatives as accels. of vulc.

Romani, E. (3) Furfuramide with S and H<sub>2</sub>S or furfural with (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub> gives dithiopyromucic acid. See Dithio-acids. A mixture of R, ZnO, S and "Vulcazol" will vulc. rapidly in an atmosphere of H<sub>2</sub>S at 100° C.

Rosenbaum, J. L. (1).

Schidrowitz, P. (22) Liable to decomposition.

Twiss, D. F. (12) Graphs for R-90, S-10, Acc.-1 with and without ZnO. ZnO is needed as an inorg. accel.

**Furfurine.**

Dubosc, A. (54).

Ricard, E. (1) Accel. patent.

Schidrowitz, P. (22) More stable than furfuramide.

**Furfuro-benzidine.****Furfuro-benzylamine.****Furfuro-m-cresylene diamine.****Furfuro-dianiline.****Furfuro-dimethylaniline.****Furfuro-diphenylamine.****Furfuro-monomethylaniline.****Furfuro-beta-naphthylamine.****Furfuro-phenyl hydrazine.****Furfuro-piperidine.****Furfuro-toluidine.****Furfuryl-amine.****Furfuryl-antioxime.****Furfuryl-synaldoxime.****Mono-furfuryl-aniline.****Nitroso-furfurine.****Oxy-furfuraniline.**

Dubosc, A. (54) Accels. of vulc.

Ricard, E. (1) Accel. patent.

**Gases. Absorption, diffusion and solubility in Rubber.** See Carbon Dioxide, Hydrogen.

Aronstein & Sirks. (1) R. dipped in hot linseed oil for 2 hrs. almost impermeable, dipped in asphalt dissolved in tar, completely impermeable to gases.

d'Arsonval. (1) Action of CO<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub> on R. Nitrogen suggested for inflation of tires due to slow diffusion.

Asano, K. (1) CO<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>, air or O<sub>2</sub> have no appreciable influence on crude R. in absence of light up to 70° C. CO<sub>2</sub> decreases polymerization and protects against tackiness.

Cagniard-Latour. (1) Diffusion of H<sub>2</sub> gas thru R.

Chappius, P. (1) R. shows characteristic properties of a liquid in the absorption of gases. Action of methylchloride on R.

Ditmar, R. (44) Absorption of gases by R.

Edwards, J. D. & Pickering, S. F. (1) Permeability of R. to H<sub>2</sub>S, O<sub>2</sub>, N<sub>2</sub>, Argon, Air, CO<sub>2</sub>, He, NH<sub>3</sub>, Ethyl chloride, Methyl-chloride and steam.

Graham, T. (1) Diffusion of a gas through R. depends on a chemical affinity, a solution of the gas results. A liquid passes through R. more readily than a gas. Liquids and colloids such as R. have no pores and even in a thin film are impermeable to gases.

Grosheintz, K. (1) Absorption and diffusion of coal gas by R. The smaller the amount of mineral matter the more pronounced is the action.

Grünmach, L. (1) Factors affecting the diffusion of CO<sub>2</sub> through R.

Hempel, W. (2) Vulc. R. acts like a liquid toward CO<sub>2</sub> and nitrous oxide and allows them to diffuse through.

Hüfner, G. (1) At 5° to 25° C. there is no definite absorption coefficient of air through gray vulc. R. At 15° to 25° C. no measurable amount of nitrogen is absorbed by gray vulc. R. At -2° C. R. absorbs an equal volume of dry CO<sub>2</sub>, the absorption coefficient decreases with rise of temp. From -2° C. to +13° C. hydrogen behaves like nitrogen.

Kayser, H. (1) Diffusion of CO<sub>2</sub> and H<sub>2</sub> through R. at 0° C. is zero.

Payen, M. (3) The porosity of R. plays a rôle in the dialysis of gases in the same manner as the porosity of membranes does in the phenomenon of endosmosis.

Peyron. (1) Air, H<sub>2</sub>, nitrous oxide and CO<sub>2</sub> easily diffuse through R.

Reychler, A. (1) SO<sub>2</sub> and CO<sub>2</sub> diffuse through R. more rapidly than other gases because of strong affinity for R. Referred to as an occlusion phenomenon. True diffusion process proceeds more slowly.

Terry, H. L. (7) Ammonia, carbonic acid and air pass through R. faster than nitrogen or carbon dioxide.

Wroblewski, S. v. (1) Henry-Dalton's absorption law for liquids and gases holds for R. and gas. Absorption of NO, CO<sub>2</sub> and H<sub>2</sub> by R. is purely a physical process. Gases absorbed by R. retain their gaseous state. (2) Speed of diffusion of a gas through a R. membrane is proportional to the pressure of the diffusing gas on the membrane. Effect of CO<sub>2</sub> and H<sub>2</sub>.

Zulkowsky, K. (1) The illuminating power of lighting gas is lowered by R. tubing.

**Gas Black.** See Carbon, Lamp Black.

Anon. (42) Use of gas black in tires. (44) Gas black decreases time of cure, toughens the stock and increases tensile strength, stretch and durability.

Dubosc, A. (59) Gas black gives a compound of lower sp. gr., faster curing, higher tensile strength and elasticity than a similar ZnO compound.

Pickles, S. S. (6) A moderate accel. of vulc.

**Gelatin.** See Glue.

**Geraniol.**

Ostromuiskii, I. (13) & (22) A weak accel. when used with metallic oxides. See Colophony and Xanthates.

**Glass.**

Ditmar, R. & Dinglinger, O. (2) Powdered glass prevents the oxidation of R.

**Glucoprotein.**

Spence, D. & Kratz, G. D. (1) See Protein.

**Glucose.** See Aldehyde-Amines.

Anon. (255) A retarder of the vulc. of R.

Bayles, E. A. (1) See Dinitrosophenol.

Girard, F. & Rose, E. (1) See Latex-Coagulants-Sugar.

King, A. H. (5).

Peachey, S. J. (11) A retarder of the vulc. of R.

**Glucose Ammonia.**

Cadwell, S. M. (3) See Aldehyde-Amines.

**Glucose Aniline.**

Cadwell, S. M. (3) See Aldehyde-Amines.

**Glue.** See Protein.

Anon. (119) Glue in R. (256) Glue and gelatine in the R. industry. Preparation and incorporation into R.

Hartong, R. C. (1) An emulsion of glue, pine oil and gas black is milled into R. (3) Wet process of mixing glue and other compounding ingredients into R.

Hornung, E. & Hansel, S. (1) See Ageing-Tackiness.

Kempel, A. D. (1) Accelerating effect is mentioned.

North, C. O. (1) A water solution of glue is admixed with pigments and emulsified with benzene prior to mixing into R.

O'Brien, W. J. (1) Direct mixing of air dried glue into R.

Schidrowitz, P. (48) Properties of glue.

Wiegand, W. B. (1) Glue gives a stiffer and tougher rubber although the tensile strength is somewhat lower.

### **Glycerol.**

#### **Glycerin.**

Anon. (166) See Ageing.

Beyer, C. (1) Treatment with glycerin preserves elasticity of R. goods.

Morellet, F. (1) Vulc. R. in boiling glycerin takes on the character of unvulc. R. and dissolves in ordinary solvents for unvul. R.

Ostromuiskii, I. (13) Accelerates vulc. of R. See Xanthates.

Terry, H. L. (10) Glycerin does not dissolve R. Its use in R. offers no special advantages.

Twiss, D. F. (2) Caustic alkalis dissolved in glycerol as accels. of vulc.

### **Glycine.**

Heilbronner, A. (1) See Tannin.

### **Glycol.**

Pickles, S. S. (4) Na & Pb salts mentioned as accels.

Twiss, D. F. (2) Alkalies dissolved in glycol as accels. of vulc.

### **Guanidine.** See Aminoguanidine.

Dubosc, A. (40) An accel.

King, A. H. (1).

Kratz, G. D., Flower, A. H. & Coolidge, C. (1).

Whitby, G. S. (8) p. 190. Guanidines act as accels. of vulc. They have been recognized in the products of putrefaction in matured R.

### **Guanylyl-Guanidine.**

#### **Biguanide.**

Dubosc, A. (40) An accel. of vulc.

### **Guanylurea.**

Anon. (54) A vulcanizing agent.

Minatoya, S. & Fukuda, S. (1) Used in Japan as an accel.

### **Guayule.**

Alexander, P. (10) Phenyl acetic acid obtained by treating guayule with alkali.  $1\frac{1}{2}$ -4% essential oil present

in guayule prevents proper vulc. Ageing of guayule plants prior to extraction.

Ditmar, R. (27) Guayule vulc. with increasing amounts of S gave continuously increasing tensiles with maximum elasticity at 35% S.

Fox, C. P. (2) See Ageing-Tackiness  
Marchwald, E. & Frank, F. (4) Obtained a normal nitrosite "C" and nitrogen peroxide addition product from guayule. Vulcanization tests.

Whittelsey, T. T. (2) Rubber and resin content of guayule.

### **Guaiacol.**

Ditmar, R. (10) See Latex-Preservatives.

### **Gutta.**

Oesterle. (1) & (2) A constituent of gutta percha, containing oxygen.

**Gutta percha.** See Ageing, Ageing-Oxidation, Ageing-Tackiness, Bromine, Chlorine, Heat, Ozone.

Adriani, A. (2) Extraction of g.p. with hot and cold alcohol. (3) Dry distillation of g. p. and analysis of the ash.

Allen. (1) p. 156-161, chemistry of g.p.  $\text{HNO}_3$  on g.p. gives formic acid and other products.

Anon. (196) G. p. does not oxidize in the dark or under water. (216) Vulc. of g.p. (281) G. p. exposed to light and air changes into a brittle resinous substance. Balata is but slowly acted upon under similar conditions.

Armstrong, J. M. (1) G. p. first introduced into England for manufacturing purposes by R. A. Brooman (1844-45).

Arppe, (1) G. p. is a mixture of the oxidation products of  $\text{C}_{10}\text{H}_{16}$ . Isolated two crystalline and four amorphous resins in g. p.

Barlow, W. A. & Forster, T. (1) G.p., New Zealand gum and sulfur mixed at  $120^\circ\text{F}$ . The S acts as preservative of the g.p. No heating was carried out at vulcanizing temp.

Baumhauer, H. von (1) Pure gutta is violently attacked by ozone. Gutta decomposes at  $180^\circ\text{C}$ . In HCl gas gutta assumes a brown black color. Found an oxygen free substance in g.p. of formula  $\text{C}_{20}\text{H}_{22}$  along with two

- substances of composition  $C_{20}H_{32}O$  and  $C_{20}H_{32}O_2$  which were not investigated further.
- Bernard, B. H. I. (1) History, preparation, properties and uses of g.p.
- Berry, W. G. (1) G.p. completely converted to resin by oxidation. Saponification number of resin serves to identify the gum.
- Bolas, T. (8) Vulc. of g.p. with  $S_2Cl_2$  or mixture of antimony sulfide and S.
- Brasse, L. (1) Early history of g.p. Effect of impurities on properties of g.p. Introduced into Europe in 1842 by Montgomery. Effect of impurities.
- Caspari, W. A. (1) Chemistry of g.p. and balata. See Balata.
- Camille, A. (21) G.p. may be vulc. with S, sulfides or  $S_2Cl_2$ . Less than 2% S is used.
- Collins, J. (1) G.p., its history and commerce.
- Dick, R. (1) R. is added to g.p. for convenience in processing.
- Ditmar, R. (12) Historical and analytical. Separation of alban, albanan and fluavil. (45) Presence of fluavil does not diminish quality of g.p. Alban and albanan in large amounts indicate poor quality. (56) Change in softening point of g.p. by added materials. (60) Vulc. of g.p. resins.
- Englehard, G. H. & Day, H. H. (1)  $Cl_2$  on g.p. gives a white hard product.
- Fol, J. G. (6) Comparison of the leaf and stem g.p. of the two Tjipetir varieties. Resin and ash content of stem g.p. is higher than of the leaf g.p.
- Frank, F. & Marckwald, E. (1) G.p. like substance in resins of Karite tree gave a nitrosite similar to Harries' Nitrosite "C."
- Hancock, C. (1) Sulfurated or unsulfurated g.p. or R. improved by exposing to oxides of nitrogen or immersing in hot conc.  $ZnCl_2$  solution. (3) G.p. and S or metallic sulfides vulc. at high temperatures. (4) Treatment of g.p. in a salt bath of  $Na_2CO_3$ ,  $CaCl_2$ ,  $NaOH$ ,  $Na_2S$  or etc.
- Harries, C. (10) G.p. gives quantitative yield of diozonide,  $C_{10}H_{16}O_6$ . Products of hydrolysis are similar to those of R. but in different proportions. (11) See Laevulinic Acid. (31) p. 117.
- Havemann, R.F.H. (1)  $Cl_2$  on g.p.
- Heckel, F. & Schlagdenhaufen, Fr. (1) Chemical description of Abyssinian g.p.
- Hillen, G. H. (1) Resins of g.p. from German New Guiana consist chiefly of lupeol cinnamate and an oily substance resembling that found in Chicle gum. Resin of Malalauvai g.p. consists chiefly of alpha- and beta-amyrin acetate, an oleaginous substance and a yellow resin.
- Hoffman, A. W. (1) Fresh g.p. is free from oxygen, oxidized g.p. contains 28%  $O_2$ . (2) Changes of g.p. under tropical influences.
- Jungfleisch, E. & Leroux, H. (1) Pal-treubin,  $C_{30}H_{50}O$ , m.p.  $260^\circ C$ . found in g.p. from Palaquium Treubi, which is isomeric with the amyrins.
- Kent, E. N. (1) Solubility and methods of purifying g.p.
- Lagarde, (1) Effect of temp. and water on insulating properties of g.p. The higher the gutta content and the less the resin content the poorer are the insulating properties of g.p. Presence of a minimum water content is emphasized since it aids the conversion of gutta to the resins.
- Lichtenberg, O. (1) The hydrohalogenides of g.p. were regenerated with pyridine and the regenerate was treated with  $HCl$ ,  $HBr$ ,  $N_2O_5$  and ozone. The products are similar to those obtained from R.
- MacLagan, D. (1) The oil from dry distillation contained C-86%, H-12.15% and was similar to that obtained from R. Found oxygen present in g.p.
- Marckwald, E. & Frank, F. (2) Determination of g.p.
- Meyer, L. O. P. (14) Low water and resin content makes g.p. age better.
- Miller, W. A. (1) Alternate wetting and drying causes rapid deterioration of g.p.  $O_2$  is absorbed, the weight increases and it becomes soluble in alcohol and dilute alkalies. Data on exposure tests under various conditions of light, air, water, etc. Analysis of.
- Montgomery, Wm. (1) History of the introduction of g.p. into England.



- Montpelier, J. A. (2) G.p. is a mixture of three resins, gutta  $C_{20}H_{32}$ , fluavile  $C_{20}H_{32}O$  and albane  $C_{20}H_{32}O_2$ . G.p. oxidizes in the air. Decomposed by  $HNO_3$ . Formic acid and HCN are formed. HCl converts it into a brown substance. Fluavile, strong alkalis, weak acids and conc. HCl are without effect on g.p. (3)  $H_2SO_4$  attacks g.p. in the cold liberating  $SO_2$ . Fuming  $HNO_3$  attacks g.p. liberating nitrogen peroxide and produces among other substances formic acid and HCN. HCl attacks it slowly, making it friable. HF does not attack it. Alkaline or saline solutions do not attack g.p. (4) Review of M. Payen's work. Methods of examination of g.p.
- Obach, E. F. A. (1) Ozone readily attacks g.p. Conc. HCl, acetic acid or  $NH_3$  have no appreciable action. (2) A history of g.p.
- Oesterle, O. (1) Bromine added to  $CHCl_3$  solution of gutta evolves HBr in the cold. Brominated gutta shows improved electrical properties. An aqueous solution of HCl does not attack it, but heated in a sealed tube at  $180^\circ C$ . it becomes hard and brittle. No nitrosol chloride derivative was obtained. See Guttan. (2) Constituents of g.p. Gutta ( $C_{20}H_{36}$ ), oxidized gutta, alban ( $C_{20}H_{34}O_2$ ), fluavil ( $C_{10}H_{16}O$ ), guttan, tannin, salts and sugars. Heating g.p. with  $HNO_3$  gives HCN.
- Oudemans, A. C. (1) Analysis of g.p. Pure gutta heated with conc.  $HNO_3$  forms HCN and formic acids.
- Payen, M. (1) Isolated gutta,  $C_{20}H_{32}$ , fluavil an amorphous resin,  $C_{20}H_{32}O$  and alban a crystalline resin  $C_{20}H_{32}O_2$ . Alteration in air and light is due to oxidation of gutta to fluavil and alban. Strong HCl slowly attacks g.p. at  $20^\circ C$ . rendering it hard and brittle.
- Peachey, S. J. & Skipsey, A. (3) Vulc. of g.p. by Peachey process.
- Ostwald, Wo. & Ostwald, Wa. (1) Prevention of hardening and oxidation by use of amines, alkaloids, etc.
- Ramsay, W. (1) G.p. rendered harder, tougher and more resistant by heating under pressure at  $180^\circ$  or  $200^\circ C$ . for 12 hours with 5% HCl, or with NaCl,  $CaCl_2$  or water.
- Ramsay, Chick & Collingridge. (1) Action of  $O_2$  and Br on g.p. Destructive distillation.
- Razmann, R. (1) A review of the researches on g.p. Duvivier & Chandel in 1855 used 5-15%  $S_2Cl_2$  on g.p. and obtained soft, semi-hard or hard vulcanized products. Conc.  $HNO_3$  gives a yellow product insol. in water. A small amount of HCN is given off but no formic or oxalic acid.
- Rider, W. E. (1) G.p. vulc. by incorporating a hyposulfite with or without metallic sulfides, or with or without whiting or MgO, and heating at  $285^\circ$  to  $320^\circ F$ .
- Riess, P. (1) Action of air on g.p. See Ageing.
- Rombourgh, P. van. (1) Isolated an amorphous substance from g.p. of Dutch New Guinea which yielded cinnamic acid on hydrolysis. Two esters of cinnamic acid found in resin of g.p. from Palaquium calophyllum. G.p. from Payena Leerii does not contain cinnamic acid esters. (2) See Lupeol.
- Sahlfield, F. (1) Resins of g.p. are not readily saponifiable. Constitution and properties of Alban,  $C_{20}H_{32}O_2$ . All g.p. resins form oils on dry distillation.
- Sharpe, G. H. (2) G.p. used as lining for dil.  $HNO_3$  containers in refining of gold. Daguerrotypist uses it because of its resistance to iodine and bromine. G.p. useful for fluoric and muriatic acid containers.
- Schmidt, E. A. (1) Dry distillation of g.p. gives the same products as from R.
- Scholz, V. (1) Purification with phenols.
- Schon & Son. (1) Purification of g.p. with aniline and caustic.
- Schwanert. (1)  $HNO_3$  dissolves g.p. on boiling; the addition of water precipitates a yellow resin; ultimately cmphretic acid and decomposition products of albumin are formed.
- Schwerdtfeger. (1) G.p. dissolves in  $CHCl_3$  while R. only swells to a jelly like mass.

- Siemens, C. (2) Werner Siemens discovered the use of g.p. for insulating wires in 1847.
- Siemens, C. & Halske. (1) See Chlorinated Rubber.
- Siemens, E. W. v. (1) (2) Used g.p. for electrical insulation of subterranean telegraph wires. Designed a machine for continuous coating of the wire with g.p.
- Soubeyran. (1) The dry distillation products of g.p. and R. are identical. Conc.  $\text{H}_2\text{SO}_4$  chars it.  $\text{HNO}_3$  gives a yellow product. Water, alcohol, alkalis and acids do not affect it. Analysis of g.p.
- Spence, D. (11) Karite gutta resembles R. more than g.p. Resins are hard and amorphous. They give cinnamic acid on hydrolysis.
- Spence, D. & Young, J. (2) Rate of combination of S with g.p.
- Tschirch, A. (3) Constitution of g.p. resins.
- Tschirch, A. & Müller, O. (1) G.p. from New Guiana.
- Tschirch, A. & Schereschewski, E. (1) See Balata.
- Williams, C. G. (1) Destructive distillation of g.p. gives isoprene and caoutchene.
- Halogens.** See Bromine, Chlorine, Iodine, Tetrabromide of Rubber.
- Heat.** Action on Rubber. See Ageing, Ageing-Oxidation, Ageing-Tackiness, Light, Polymerization.
- Anon. (74) (136) Action of heat on R. (307) Vacuum drying at high temp. deteriorates R.
- Axelrod, S. (1) Heating R. diminishes tensile, increases elongation and increases the rate of reaction with S.
- Breuil, P. (15) Effect of temp. of vulc. on tensile, elongation and compression of various compounds.
- Caspari, W. A. (1) Gutta softens at 55-60° C., decomposes at 185-190° C.
- Eaton, B. J. (16) Drying R. at high temp. retards vulc.
- Fendler, G. & Kuhn, O. (1) R. previously heated dissolves easily in solvents to a less viscous cement.
- Gorter, K. (7) Heated R. in air and hydrogen at 60° C. for one month. The sample in air was very tacky, while in hydrogen there was no change. Gorter believes this to be an oxidation effect.
- Minder, J. (5) Heat alone does not oxidize R. but renders it tacky.
- Schidrowitz, P. (6) p. 136. Excessive heat during drying period causes tackiness.
- Seeligmann, T., Torrilhon, G. L. & Falconnet, H. (1) p. 203. Vulc. R. is pliable at 0° C. and behaves the same on heating. More stable to high temperatures than crude R.
- Tuttle, J. B. (3) Effect of heat on vulc. R.
- Vernet, G. (2) Effect of heat on R.
- deVries, O. (14) See Sulfur-Coefficient. (24) p. 101. Heating coagulum lowers the properties of the R.
- deVries, O. & Hellendorn, H. J. (4) Heating latex injures the R. Heating dry R. lowers tensiles but does not change rate of cure. Oxidation proceeds rapidly at 85° C. See Latex.
- Weber, C. O. (17) "Heating" of R. during storage. Low grade rubbers heat up more rapidly.
- Worneley, P. L. (1) Effect of temp. on physical tests. Tensile not affected as much as elongation.
- Worthington, J. V. & Hyde, A. W. T. (1) Heat treatment of raw R. to lower viscosity.
- Heptaldehyde.** See Aldehyde-Amines and Heptylidene Aniline.
- Cadwell, S. M. (3) Aldehydes are milled into R. and act as accels. by first reacting with basic constituents present in the R.
- Heptaldehyde-benzylamine.**
- Heptaldehyde-diethylamine.**
- Heptaldehyde-monoethylamine.**
- Heptaldehyde-monomethylamine.**
- Heptaldehyde-naphthylamine.**
- Heptaldehyde-p-toluidine.**
- Heptylidene (Poly)aniline.**
- Cadwell, S. M. (3) See Aldehyde-Amines.
- Heptaldoxime.**
- Cadwell, S. M. (3) See Aldehyde-Amines.

**Heptylidene Aniline.**

Cadwell, S. M. (3) Equal mols of heptaldehyde and aniline are heated to 140° C. with 5% S. The product has high curing power, ages well and does not scorch. See Aldehyde-Amines.

**Heveene.****Hevene.**

Bouchardat, A. (1) See Distillation of Rubber.

**Hexahydroxybenzene methylinositol.**

Eaton, B. J. (26) Present in Hevea latex.

**Hexalin.**

Jones, F. (1) Properties and uses as a R. solvent.

**Hexamine Cobalt Chloride (Sulfo-carbonate).**

Dubosc, A. (15) An accel.

**Hexamethyleneamine.**

Ostromuiskii, I. (14) (31) This accel. or its dithiocarbamate is used with PbO for vulc. at low temp.

**Hexamethylenetetramine.****"Hex."****"Hexa."****"Urotropine."**

Anon. (84). (308) "The most useful all around organic accel." Method of handling, compounding tests, etc.

Bayer & Co. (19) An accel. of vulc.

Bedford, C. W. (2) Hexa is dispersed on ZnO or S to get better distribution in the R. (4).

Bedford, C. W. & Scott, W. (1) S reacts with Hexa during vulc., forming  $\text{NH}_3$ ,  $\text{H}_2\text{S}$  and  $\text{CS}_2$ .

Boutaric, J. (1) Used hexa as devulcanizing agent for R.

Cranor, D. F. (1) Physical and chemical data on Smoked sheet cured with and without Hexa. See Sulfur-Coefficient of Vulcanization.

Dannerth, F. (1).

Davies, E. L. (2) Hexa is the best accel. to use with clay. The R. T. Vanderbilt Co. also recommends Super Sulfur No. 2.

Depew, H. A. (1) Effect of varying amounts of S and Hexa on properties of vulcanizate.

Dubosc, A. (30) Hexa reacts with S during vulc. forming  $\text{H}_2\text{S}$ , acetylene and sulfocyanic acid. (33) (34) & (41) Devulcanization by the aid of Hexa. Sc was reduced from 2.667% to 1.195% with hexa in alcoholic solution. Aniline did not remove an appreciable amount of S. Alternate treatment with  $\text{HCHO}$  and  $\text{NH}_3$  under pressure removed over 90% of combined sulfur. (40) Hexa-nitrate. (42) Sulfur reactions of hexa. All amino accels. give  $\text{CS}_2$ ,  $\text{H}_2\text{S}$  and HSCN during vulc.

Earle, D. (1) Poisoning by accels.

Endres, H. A. (1) Comparison of the curing power of hexa and several other accels.

Geer, W. C. (2). (5) p. 48.

General Rubber Co. (3) See Latex-Preservatives.

Greider, H. W. (1) Use with  $\text{MgO}$ .

Herzog, W. (1) Method of manufacture.

Luff, B. D. W. (1) Found thiocyanic acid in R. which had been cured with hexa.

Murrill, P. I. (5).

Ostromuiskii, I. (13) An accel. (22) Hexa and ZnO used in curing synth. R.

Peachey, S. J. (2).

Pearson, H. C. (1) p. 84.

Pickles, S. S. (3) Hexa is strongly activated by ZnO. (4) General discussion on accels.

Plauson, H. (1) Manufacture of hexa by oxidizing methane in the presence of  $\text{NH}_3$ .

Rosenbaum, J. L. (1) R-50, ZnO-45, S-3, Hexa-0.5. Cure 20 Min./45 lbs. to Sc=0.62; Cure 40 Min./45 lbs. to Sc=1.30. These two cures give practically the same physical properties. See Sulphur.

Sander, A. (1) Method of manufacture.

Scott, W. & Bedford, C. W. (1) Hexa reacts with S during vulc. to form ammonium polysulfide and ammonium dithiocarbamate.

Schidrowitz, P. (19).

Shepard, N. A. & Krall, S. (1) Prevention of rash produced by hexa.

- Simmons, H. E. (1).  
 Shepard, N. A. & Krall, S. (2) Reproduction of the same stress strain curves by the use of various accels. Hexa, p-nitrosodimethylaniline, aldehyde ammonia and thiocarbonyl. Tuttle, J. B. (1) Graphs for R-48, ZnO-48, S-3, Hexa-I. Cures at 287° F.  
 Twiss, D. F. (12) Graphs for R-S-hexa stocks containing low amounts of ZnO, Clay and gas black. Discontinuity in elongation curves.  
 Twiss, D. F. & Brazier, S. A. (1) R-90, S-10, Hexa-0.5. ZnO has strong accelerating action on hexa.  
 Twiss, D. F. & Howson, C. W. H. (1) R-90, S-10, ZnO-1, Hexa-1. Cures at 118° and 138° C. A point of inflection is found in tensile, elongation and coefficient curves.  
 Weber, L. E. (9) A popular accel. 1½% is the upper limit. ZnO is desirable but not necessary. May be used with antimony sulfides.  
 Whitby, G. S. & Walker, O. J. (1) Comparison of hexa with piperidinepentamethylene-dithiocarbamate in R-90, S-10.  
 Williams, C. S. (1) Tables of testing data on various compounds. (2) Effect of varying S and hexa in R-100, ZnO-3. Cures at 298° F. 1% hexa and 3% S are recommended.
- Hexamethylenetetramine acid nitrate.**  
 $C_6H_{12}N_4 \cdot 2HNO_3$ .  
 Dubosc, A. (47).
- Hexamethylenetetramine neutral nitrate.**  
 $C_6H_{12}N_4 \cdot HNO_3$ .  
 Dubosc, A. (47).
- Hexamine Cobalt Sulfocarbonate.**  
 Dubosc, A. (40) An accel.
- Hexanitrodiphenylamine.** See Aurantica.
- Historical.**  
 Anon. (1) History of rubber and its discovery. (2) Early rubber experiences of Charles Goodyear. (6) Polemical on the discovery of gutta percha covered wire. (7) History of the waterproof industry. (9) History of rubber to 1901. (10) Life of Charles Goodyear. (12) Historical and descriptive account of the rubber industry. (15) Development of hose. (19) Founders of the rubber industry; I Thomas Hancock, II Charles Goodyear, III & IV Charles Mackintosh. (20) History of rubber tiling and paving. (21) History of the cable industry. (22) History of rubber boots and shoes. (23) History of the waterproof industry. (24) History of rubber hose. (25) History of belting. (26) History of golf balls. (27) History of tires. (28) History of rubber heels. (29) History of rubber machinery. (30) Chronological history of the rubber trade. (55) History of the vulcanization of rubber with special reference to Charles Goodyear, Thomas Hancock and Stephen Moulton. (61) Pioneers of the R. trade. N. Hayward, Chas. Goodyear, Wm. A. Buckingham, H. G. Tyler, Chas. Mackintosh, H. Mattson, D. Hodgmann, T. J. Mayall, B. M. Hotchkiss. (63) An account of the experiments of N. Hayward with R. and S. (71) The work of Chas. Mackintosh, Thomas Hancock and Charles Goodyear. (72) Development of the hard rubber industry. (89) Résumé of R. pavements. (184) History of the vulcanization of R. (188) 18 patents by Johann Nepomuk Reithoffer from 1824 to 1846 on the use of R.  
 Armstrong, J. M. (1) History of gutta percha industry in the U. S.  
 Bronde, W. T. (1) See Chlorine and Mineral Rubber.  
 Camille, A. (22) Pioneers in waterproof fabric development and the vulc. of R.  
 Chapel, E. (1) Good historical résumé.  
 Davis, C. (1) History and properties of caoutchouc.  
 Dubosc, A. (4) Life and work of la Condamine and his associates.  
 Dunlap, J. B. (1) History of rubber vulcanization.  
 Frankenburg, S. (1) Development of rubber and the rubber industry.  
 Geer, W. C. (5) p. 9 & 24. Discovery of vulc. by Goodyear. S and White lead. Jan. 1839. p. 26. Brockendon, an assistant of Hancock, first used the term "vulcanization." See review by M. M. Miller, I. R. R. Oct. (1922) p. 28.

- Geuns, J. van. (1) Ascribes discovery of vulc. to Thos. Hancock. See W. P. Jorissen (2).
- Gottlob, K. O. (3) Development of the R. industry.
- Grossman, F. (2) Fifty years of German rubber science.
- Hancock, T. (7) Used the word "vulcanization" in patent in 1845. (8) Vulc. of R. in molds, patented in 1846.
- Lock, R. H. (1) History of R. in Ceylon from 1876 to date.
- Meyer, L. O. P. (2) Patents on vulcanization issued in U. S. in 1859-60 and in England prior to 1860. (3) Life and work of Charles Goodyear.
- Moulton, J. C. (2) History of the R. industry, the part played by Stephen Moulton and his successors. (3) The work of S. Moulton.
- Pahl, W. (1) History of R. History of vulcanization with a discussion of the applications of R. for various uses.
- Pavoux, E. (1) Description of manufacturing processes and vulcanization prior to 1874.
- Perkin, F. M. (1) History of rubber and gutta percha.
- Pinto, P. (1) History of R.
- Porritt, B. D. (5) History of R.
- Rogers, H. (1) Review of R. manufacture.
- Rossem, A. van. (9) Description of Thos. Hancock's inventions and early development of the R. industry. (10) Historical review of vulcanization processes and development of the manufacture of R.
- Sarcey, F. (1) Fresnau while in S. A. made the first pair of R. boots.
- Schulze, E. (2) Development of the water proofing industry. (10) History of the rubber companies operating in 1862 and the products made by them.
- Siemens, C. (2) E. W. Siemens in 1847 discovered the use of gutta percha as an insulator for copper wire.
- Thenard, L. J. (1) See Chlorine.
- Thomson, R. W. (1) First patent for a pneumatic tire (1845).
- Vincent, E. (1) Historical review of R. prior to 1858.
- Weber, C. O. (10) History of vulc.
- Weinberg, A. (1) History of R. Résumé of researches on R.

**Chronological Survey**

1521. d'Anghiera, Pietro Martire, (1) First mention of the word rubber in the literature.
1536. Gonzalo Fernandés d'Ovièdo y Valdes, (1) Describes the North American Indian game of ball called "Batey."
1601. Antonio de Herrera Tordesillas, (1) Describes the game played by the natives of Haiti with balls made of rubber. Mentions presence of trees in Mexico which when tapped yield a milk from which rubber may be obtained.
1615. Torquemada, F. Juan de, (1) Describes the Mexican Indians as making shoes, headgear, clothing and other water tight articles from the gum obtained from the milk of a tree.
1656. Tradescant, John, issued a catalog of the rarities preserved at South Lambeth, wherein is given the earliest notice of the appearance of gutta percha in England under the name "Mazer Wood." Anon. (60).
1733. Charlevoix, Xavier de, (1) Describes Batos as being a special ball of solid matter which is very light and porous.
1736. Condamine, Charles Marie de la, sent the first samples of rubber from Peru to the French Academy in Paris and described its properties. Anon. (60).
1755. Don José, King of Portugal, sent his boots to Para to be waterproofed.
1763. Herissant, L. A. P. & Macquer, P. J., (1) Researches on solvents for rubber.
1768. Macquer, P. J., (1) Solution of rubber in ether.
1770. Priestley, J., used rubber to erase lead pencil marks. Anon. (288).
1781. Bernard, R., (1) A study of the oil obtained by the dry distillation of rubber. Fanjas de St. Fond., described a bitumen obtained from the mines of Castleton in Derbyshire and called mineral rubber.
1785. Professors Charles and Robert made ascensions in the first balloon which was filled with hydrogen

- gas. The gas envelope was of silk coated with rubber that had been dissolved in turpentine.
1791. Grossart, Chirly, (1) Describes the construction of tubes of caoutchouc by rolling strips of caoutchouc around glass cones or cylinders. The caoutchouc was first immersed in ether or essential oils.
- Peal, S., (1) First known caoutchouc patent. Used rubber dissolved in turpentine or rubber latex to waterproof leather, cotton, linen, woolen cloths, etc.
1797. Johnson, H., (1) Prepared waterproof cloth with rubber dissolved in spirits of turpentine and spirits of wine. The odor of turpentine was removed by oil of wormwood. Tackiness was prevented by dusting with wool or silk powder.
1798. *Ficus elastica*, the first Asiatic rubber producing plant, became known when Howison discovered *Urceola elastica*. Anon. (270) & (288).
1800. First importation of bottle rubber from Brazil to the U. S. Anon. (60).
1803. A factory for the manufacture of elastic rubber bands or braces was erected at St. Denis near Paris. Anon. (60).
1805. Specimens of East India rubber plant, *Ficus-repens*, first introduced into Great Britain. Anon. (60).
1808. Landale suggested a new process of engraving upon glass upon which he had previously spread a thin coating of rubber. Anon. (9).
1811. Champion directed his attention to waterproofing materials for the French Army. Anon. (9).
1813. Clark, J., (1) Manufacture of inflated beds, pillows, cushions, by means of a solution of rubber in organic solvents. Hummel, J. F., obtained a U. S. patent for a gum elastic varnish. Anon. (60).
1818. Prof. Syme used coal tar distillate of gravity 0.770 (probably benzene) as a solvent for rubber prior to Macintosh. Anon. (11).
1819. Hancock, Thos., began experimenting with rubber. First attempt to dissolve rubber in turpentine unsuccessful. Anon. (60).
1820. Hancock, James, established first rubber factory in England. Seeligmann, Torrilhon & Falconnet (2).
- Hancock, T., Invention and development of the masticator. I.R.W. 14,293 (1896). Took out a patent on elastic fabric with rubber strips. Anon. (207). Made elastic bands for mittens, etc., and shoe soles of rubber. Anon. (60).
- Howe, J. J., U. S. patent for a mill which forms india rubber for use on cloth or otherwise. Anon. (60).
- Nadier cut rubber into threads to be used for elastic fabrics. Seeligmann, Torrilhon & Falconnet (2) & Anon. (288).
- First pair of rubber shoes imported from Para reached the U. S. Anon. (60).
1821. The Hancock hand masticator is replaced by a horse power driven machine capable of handling 15 lbs. of caoutchouc. Anon. (60).
- Syme, J., said to be first to discover a method of waterproofing by means of caoutchouc. Anon. (60).
1823. Macintosh, Chas., (1) Obtains first English patent for manufacture of waterproof double textures by means of rubber dissolved in coal tar naphtha.
- 500 pair of rubber shoes imported from Brazil into Boston. Anon. (60).
1824. Fleetwood, C. B., obtains an English patent for a waterproofing liquid consisting of rubber in pure spirits of turpentine. Anon. (60).
- Hancock, Thos., (8) Patented the use of rubber in its natural liquid state to saturate felt, cotton, wool, hair, etc., and subject the whole to pressure.
- Weise, Wm. P., (1) Obtains an English patent for a waterproofing solution made of equal parts of shellac, caoutchouc, gum mastic, gum amini, and gum sandarac in spirits of wine or turpentine.
1825. Hancock, T., (5) Preparation of waterproof cloth. (9) Use of Stockholm tar with rubber.
- Leeson, H. B., describes manufacture of tubes by wrapping strips

- of rubber around a polished tube of required diameter. Anon. (60). Wales, Thos. C., sold first lot of india rubber shoes imported from Para in Boston, Mass. Anon. (60).
1826. Hancock, Thos., manufactures gas bags for experimental purposes. Anon. (60). Lacy, H. C., English patent for carriage springs made of "cubical blocks of rubber." Anon. (60). Rattier & Guibal introduce machinery for cutting threads for manufacture of elastic fabrics, into their St. Denis factory. Anon. (60). First detailed account of heating rubber in molds is in "The Operative Mechanic," Philadelphia, p. 299. Anon. (60).
1827. Coles & Nickolson, English patent 5,465 for an elastic gasometer using rubberized fabrics. *Gummi Zt. II*, No. 3, p. 1 (1896). Manufacture of first india rubber hose by C. Macintosh & Co., Manchester. It was used in the fire at Fresh Wharf in London. Anon. (24) & (60).
1828. Comstock, of Hartford, Conn., obtains a patent for spreading a solution of rubber in turpentine on cloth. Anon. (9) & (60). Reithoffer, J. N. & Purschter, A., (June 19), patented in Vienna the preparation of cotton, silk or wool threads having a rubber center.
1829. Howe, J. J., patented the use of rubber and resins soluble in turpentine to form a paint, varnish or cement. Anon. (60). The first elastic fabric factory in Germany was started by François Fonrobert in Finsterwald in the Lansitz. Manders, A. S. (1) p. 317.
1830. Davis, Chas., (1) Describes process for combining rubber with stockinette. Anon. (60). Hancock, Thos., (8) Aug. 5 obtained an English patent for use of pure liquid caoutchouc as taken from trees, in the manufacture of "certain articles of dress or wearing apparel, fancy ornaments and figures." Colors may be added to the latex. Anon. (60). Rubber latex, inorganic materials and moist paper pulp are mixed and used to make shoes, hose, socks, mittens. *Gummi Zt. II*, No. 3, p. 1 (1896). Sends an agent to Brazil to teach natives the best method of collecting and preserving latex. Anon. (60).
1831. Chaffee, E. M., found that rubber dissolved in turpentine and lamp-black gives a varnish that gives leather or cloth a smooth, hard surface, impervious to water. *I.R.J.* 25, 20 (1903). Guthrie, Sam, Use of oil of turpentine charged with sulfur for dissolving caoutchouc. *I.R.W.* 5, 18 (1891). Richards, G. H., obtained a U. S. patent, "for a mode of rendering a variety of articles waterproof by means of fluid caoutchouc." *Franklin Journal* 8, p. 131; Anon. (60).
1832. Chaffee, E. M., invents a spreading machine. Anon. (29). Dumeste, J. F. M., obtains an English patent for the first rubber thread cutting machine. Anon. (28) & (60). Hayward, N., (1) Sulfur added to rubber in solution or rubbed on the surface causes it to dry more perfectly. Ludersdorf, F., (1) Rubber dissolved in a mixture of 3% sulfur in turpentine, which had been previously heated, showed greater stability to light and oxidation.
1833. Barnard, W. H., (1) Discovered caoutchoucine "a solvent hitherto unknown in the arts" by distillation of rubber. Hood, J. M., exhibited rubber boots made in New York which had been sent to South America to be varnished with fresh latex. Anon. (60). Roxbury India Rubber Factory, Roxbury, Mass., is chartered. Anon. (60). Ruggles, N. & Breed, S., obtain separate U. S. patents for attaching soles to boots and shoes by means of caoutchouc. Anon. (60).
1834. Chaffee, E. M., patented the first rubber boot, it was combined with leather to make it durable. *I.R.W.* 5, 42 (1891). Cooper, G. D., patented the ap-

- plication of rubber sheets to vessels and roofs of buildings to prevent leakage. Anon. (60).  
 Jones, A., applied a rubber varnish to a canvas previously covered with wall paper. Anon. (60).  
 Mackie, P., patented the covering of ropes, which are to be exposed to the weather, with a solution of rubber in purified coal tar naphtha. Anon. (60).
1835. Goodyear, Chas., removed tackiness of rubber compounded with magnesia, which had been dissolved in turpentine, by boiling the articles in quick lime and water. Anon. (60).  
 Sevier, R. W., (2) Lead acetate, PbO and zinc sulfate added to a solution of rubber.  
 Rubber cushions for billiard tables were introduced. I.R.W. 7, 16 (1892).
1836. Chaffee, E. M., took out a U. S. patent for applying undissolved rubber to cloth, leather, etc., for coloring rubber without solvent. Description of calender and mixing mill. Anon. (60).  
 Goodyear, Chas., treated surface of rubber by dipping in nitric acid. Anon. (60). Received medals from New York American Institute "for india rubber drapery not liable to decomposition from exposure in the sun." Anon. (60).  
 Hancock, Wm., applied a solution of rubber to the binding of books. Anon. (60).  
 Pickersgill, John, English patent 7,178 rolled rubber out in thin sheets and pressed them on fabric without the use of solvents. Gummi Zt. 11, No. 3, p. 1 (1896). Anon. (9) & (60).  
 Sievier, R. W., (1) Rubber dissolves in ammonia after standing for several months. Gummi Zt. 11, No. 3, p. 1 (1896). Anon. (9) & (60).
1837. Goodyear, Chas., (4) p. 165 & (5) Acid gas process (nitric acid) for vulcanizing rubber.  
 Hancock, Thos., (6) Description and details of his masticator and spreader. Gummi Zt. 11, No. 3, p. 1 (1896).
- Haywood, N., invented the wringer roll.  
 Wheatstone, planned undersea cable between England and France. Used gutta percha insulator. He had a poor union between wire and gum. See Marzahn, R. (4).
1838. Goodyear, Chas., improved manufacture of rubber by use of sulfur. I.R.W. 3, 57 (1890).  
 Hancock, T., English patent 7,556, spread fabric by first treating with starch, lime, etc., and then spread on the rubber coating. The starch was then removed with water. Talcum used to prevent stickiness. Gummi Zt. 11, No. 3, p. 1 (1896).
1839. Goodyear, Chas., (1) Vulcanized rubber with sulfur by the aid of heat.
1840. Freeman, Wm., obtains an English patent for paving roads with rubber combined with saw dust, sand or fine stone. Anon. (89).  
 Hancock, J., English patent for combining rubber with wood, whalebone or other fibrous material. Anon. (62).  
 Hodgman, Daniel, builds factory for manufacture of rubber at 26th St., East River, New York. Anon. (62).  
 Keen, Chas., patents the addition of lampblack or other color to the dough to improve appearance of waterproof fabrics. Anon. (23).
1841. Fanshaw, J. A., (1) Addition of sulfur to rubber. He used for the first time a mixture of lead oxide, sulfur and rubber, which is vulcanizable.  
 Rattier & Guibal (a French firm), received samples of caoutchouc that were unaffected by heat or cold.  
 Rogers, C. B. & Arnold, E., obtain a U. S. patent for the manufacture of rubber balls.
1842. Brockedon, showed Hancock pieces of rubber from America not affected by cold, solvents, heat or oils. Anon. (9) & (207).  
 Montgomery, Wm., (1) Introduces gutta percha into Europe.
1843. d'Almeida, brought samples of gutta percha to London. Anon. (62).



- Hancock, T., (1) Vulcanization of rubber in steam, water and sulfur bath. Used Mg silicate to prevent tackiness. Description of a calendar. *E. P.* 9,935 (1843). *Gummi Zt.* 11, No. 4, p. 1 (1896).  
 Jeffrey, M., prepares a gum lacquer by dissolving rubber in oil of naphtha or crude naphtha. *Bull. Soc. de Encouragement* 42, 93 (1843).  
 Parkes, A., Use of  $\text{CS}_2$  as a rubber solvent. *E. P.* 9,807 (1843). *Gummi Zt.* 11, No. 4, p. 1 (1896).
1844. Alsop, Wm. & Forster, Thos., make first mention of rubber for belting in a patent. *Anon.* (25).  
 Cassel, E. E., prepares a paving compound consisting of chalk, tar, rosin, liquid caoutchouc and sulfur. *Anon.* (89).  
 200 lbs. gutta percha shipped to England from Singapore. *Anon.* (62).  
 Stationer's bands are introduced. *Anon.* (89).
1845. Keene, Chas., patents the addition of sulfur to rubber boots, shoes, etc. *Anon.* (22). Vulcanized with sulfur vapors. *Anon.* (207).  
 Nickles, C., patents the use of gutta percha for book binding. See Armstrong, J. M. (1).  
 Thomson, R. W., (1) Invents a pneumatic tire consisting of one large tube expanded or several side by side.  
 First use of gutta percha in manufacture of golf balls. They were molded with a plain surface. *Anon.* (26).  
 Rubber used in surgical instruments, life preservers, gas holders, varnishes, pavements and roofing. Rubber trees planted in Florida. Report of Commissioner of Patents. *Anon.* (62).
1846. Harmon, J., softened rubber by grinding and use of turpentine or naphtha, combined with steam. *Anon.* (62).  
 Hancock, T., prepared sponge rubber with alum or  $(\text{NH}_4)_2\text{CO}_3$ . *Anon.* (62).  
 Parkes, A., (1) Vulcanization of rubber with  $\text{S}_2\text{Cl}_2$  in  $\text{CS}_2$ ,  $\text{C}_6\text{H}_6$  or turpentine.
- Siemens, E. W., (1) Started the use of gutta percha as a covering for telegraph wires.
1847. Craven, J. J., lays the first submarine wire insulated with gutta percha. *I.R.W.* 5, 42 (1891).  
 Forster, Thomas, patented the solution of rubber in alcohol and coal oil. *Anon.* (62).  
 Hancock, Chas., (3) Recommends antimony sulfide or other sulfides to vulcanize gutta percha. (4) Vulcanization of gutta percha with alkaline sulfides.  
 Moulton, S., (1) Vulcanization of rubber with  $\text{PbS}$ .
1848. Faraday noted the insulating property of gutta percha.
1849. Dalton, John, applied gutta percha to fabrics. *Anon.* (62).  
 Tyler, H. G. & Helm, J. G., (1) The mixture of zinc carbonate, zinc sulfate and other zinc salts with sulfur in a rubber mix. *Gummi Zt.* 5, No. 8, p. 1 (1891).  
*Anon.* (61) & (62).  
 Walker in 1849 first attempted a practical application of telegraph conductors insulated by gutta percha in the channel cable. *I.R.J.* 7, 124 (1890).
1850. Armstrong, S. T. & Gilbert, C. J., Lime and heat used to neutralize the acid in gutta percha. *Anon.* (62).  
 Hayward, F. D. & Bickford, J. C., Spreading of rubber by pressure on rollers onto the cloth. *Anon.* (62).  
 Pridham, J., (1) Used tin oxide with rubber and sulfur to produce black vulcanized rubber.  
 Reithoffer, J. N., Manufacture of first vulcanized rubber boots.  
 Siemens, E. W., (1) Patented an improved method of insulation. Gutta percha and sulfur on wire and cured. *Anon.* (62).  
 Trotter, J., (1) Vulcanization of rubber with zinc hyposulfite in place of sulfur.
1851. Goodyear, N., (1) Vulcanization of rubber to ebonite.  
 Moulton, S., (2) Lead or zinc hyposulfite with lead or zinc sulfide used to vulcanize rubber.
1852. Goodyear, Chas., adds coal tar to reduce cost of vulcanization of

- rubber. Patents for umbrellas, Parasol sticks, and combs. Anon. (62).
- Perrot, M., made gutta percha as fine as paper upon which lithographic impressions were taken. Anon. (62).
1853. Christopher, Wm., Improved devulcanization of rubber by macerating in alkalies or lime.
- Gerard, A., (1) Proposed alkaline sulfides for the vulcanization of thin objects.
- Gerard, G. E. M., Rubber heated to 240° will retain a greater expansion than its natural shape. Anon. (62).
- Rider, Wm. E. & Murphy, J., Gutta percha goods subjected to hydrogen gas to prevent bloom. See Armstrong, J. M. (1)
1855. Brooman, R. A., (1) Suggested caustic soda as a reclaiming material.
1858. Parmalee, S. T., patented the manufacture of belts by building two or more layers of fabric coated with rubber. Anon. (25).
1859. Hooper, Wm., patented use of india rubber for insulating electric wires. He was given the gold medal at the Paris exhibition in 1867. Anon. (21).
- First sample of balata sent to London. J.I.E.C. 11, 877 (1919).
1860. Williams, C. G., (1) Isoprene and dipentene from dry distillation products of rubber.
- Until 1860 South America, English India and Java were the only rubber producing countries. Anon. (288).
1861. Introduction of solid tires for cabs in London. Anon. (27).
1862. Leighton, J., introduced the rubber stamp.
1863. Humphrey, E. P., 3,183 (1863), replaces CS<sub>2</sub> of Parke's process with petroleum spirit.
1864. Spiller, J., (1) Earliest recorded work on oxidation of rubber.
1865. Hurtzig, F. & Hurtzig, Th., (1) Preparation of ivory like materials from chlorinated rubber.
1866. Forster, (1) Mercuric sulfide as a rubber pigment.
- Gerard, A., (1) Noted the presence of sugars in various kinds of rubber.
- 1867- Newbrough, J. B. & Fagan, E., (1)
1869. Vulcanization of rubber with halogens.
1870. MacCartney, dissolved rubber in warm camphor.
- Stewart, Lawrence, patented wheels for carriages and other vehicles, of vulcanite, also writing pens.
1871. Stewart, Capt., made a golf ball with a rubber core and gutta percha cover. Anon. (26).
1872. Thomas, F. S., used rubber in combination with pitch, ashes, granite, etc., for making roads, floors, etc.
- 1875- Bouchardat, G., (1) Caoutchouc
1879. and dipentene from isoprene.
1876. Foundation of plantation rubber industry in Ceylon.
1878. Abbott, Wm., (1) Patented the vapor cure with S<sub>2</sub>Cl<sub>2</sub> and neutralizing the acid with ammonia.
1880. Jenkins, A. B., Diatomaceous silica or infusorial earth mixed with rubber or gutta percha. I.R.W. 5, 9 (1891).
- Mixture of rubber and cork used as a floor covering. Manufactured by Britannia Rubber & Kamptulicon Co.
1881. Rowley, T., (1) Vulcanization of rubber in an atmosphere of ammonia.
1883. Moseley, Chas., E.P. 5,207 (1883), printing on a rubber surface previously coated with farina. Anon. (23).
1884. Moureley, (1) Vulcanization of rubber with sulfur in a 12% ammonia solution or in ammoniacal vapors.
- Tilden, W. A., (1) Prepared caoutchouc and dipentene from turpentine.
1885. Dick, R., E.P. 12,254, patents the use of gutta percha for belts. Anon. (25).
- Africa begins to export rubber. Anon. (288).
1887. Wallach, O., (1) Caoutchouc from isoprene.
1888. Dunlop, J. B., E.P. 10,607 (1888), patents the pneumatic tire. I.R.J. 1, 82 (1890).
- Gladstone, J. H. & Hibbert, W.,

(1) First important work on the chemical nature of rubber.  
Neesen, Oscar, Preparation of an elastic container for liquids. D.R. P. 43,457; Gummi Zt. 2, No. 11, p. 4 (1888).

1889. Bartlett, W. E., invents the "clincher" type or the first detachable pneumatic tire. Anon. (27).

1898. Parkin, J., suggested the use of acetic acid as a latex coagulant.

#### **Hydrazobenzene.**

Kratz, G. D., Flower, A. H. & Shapiro, B. J. (1) Has no basic properties. Is not an accel. See Aniline.

#### **Hydriodic Acid.**

Barrows, F. E. (2) Discussion of Berthelot (1).

Berthelot. (1) R. and gutta percha change to a saturated hydrocarbon which is completely hydrogenated, on heating with HI. The product is a solid and does not boil until 360° C.

Dubosc, A. & Luttringer, A. (1) p. 172. C. O. Weber did not get the HI derivative of R.

Harries, C. (24) The dihydroiodide of R. is a white product which quickly colors brown and then black ( $C_{10}H_{16}I_2$ ). Splits off iodine at 108° C. and decomposes at 125°-135° C.

Hinrichsen, F. W. & Memmler, K. (1) p. 50.

Hinrichsen, F. W., Quensell, H. & Kind-scher, E. (1) Prepared the mono-hydroiodide of R. ( $C_{10}H_{16}HI$ ). See Hydrochloric Acid.

Ramsay, Chick & Collingridge. (1) Action of HI on gutta percha.

Tassilly, E. (1) p. 313.

Weber, C. O. (14) Was unable to prepare R. hydroiodide.

#### **Hydrobenzamide.**

Dubosc, A. (54) An accel.

Eaton, B. J., Grantham, J. & Day, F. W. F. (1) An accel.

Peachey, S. J. (2) Less active than benzylidene aniline, aldehyde ammonia or "accelerene."

#### **Hydrobromic Acid.**

Dubosc, A. & Luttringer, A. (1) p. 172. C. O. Weber was unable to prepare the HBr derivative of R.

Harries, C. (24) The dihydrobromide of R. ( $C_{10}H_{16}Br_2$ ) is a white to brownish product decomposing at 160° C. (31) p. 18, 77, etc., R. regenerated from its hydrohalogenides.

Hinrichsen, F. W. & Memmler, K. (1) p. 50.

Hinrichsen, F. W., Quensell, H. & Kind-scher, E. (1) Prepared the dihydrobromide of R. See Hydrochloric Acid. Ostromuiskii, I. (10) See Bromine.

Seeligmann, Torrilhon & Falconnet. (1) p. 132. Like the organic acids, HBr has no action on R.

Staedeler. (1) No action on gutta percha. This was the beginning of the gutta percha bottle industry to transport hydrofluoric acid.

Staudinger, H., Kreis, W. & Schilt, W. (1) Action of HBr on isoprene.

Tassilly, E. (1) p. 313.

Weber, C. O. (14) Was unable to prepare the R. hydrobromide.

**Hydro Caoutchouc.** See Hydrogen.

#### **Hydrochloric Acid.**

**Rubber Hydrochloride.** See Latex-Coagulants.

Anon. (130) The hydrochloride of R. is insoluble in  $CHCl_3$ .

Blossam, T. M. (1) HCl and HCl gas have no action on R.

Caspari, W. A. (1) Gaseous HCl acts on gutta and balata giving products easily soluble in  $C_6H_6$  and  $CHCl_3$ . They begin to decompose at 185° C. Rubber gives a product insoluble in  $C_6H_6$ .

Dubosc, A. & Luttringer, A. (1) p. 171. Dry and moist hydrochloric acid act differently on R. (1) p. 172. Hot HCl used in reclaiming forms a rubber hydrochloride insoluble in ordinary solvents. This is converted into a more soluble form by heating with acetic acid.

Eaton, B. J., Grantham, J. & Day, F. W. F. (1) HCl retards the cure of matured R.

Gottlob, K. O. (6) p. 6. An addition product  $C_{10}H_{16}.2HCl$ , is obtained by passing HCl gas into a  $CHCl_3$  solution of R. Heated to 40° C., 1 molecule of HCl is given off with formation of a monohydrochloride.

- Harries, C. (18). (21) Vulc. R. is reclaimed by regeneration from its hydrochloride. (24) Rate of reaction of HCl and R. slower than for chlorine. HCl removed from the hydrochloride by heating with pyridine. Chlorine free R. obtained by treating with NaOH. Gutta percha hydrochloride contains 34% chlorine. Decomposes at 200° C. On treating with pyridine and NaOH it resembles R. more than gutta percha. Addition and splitting off of HCl changes R. to a different hydrocarbon, "Regenerat I," but having rubber like properties. Ozonide of the latter gives products not in agreement with 8 carbon ring and the R. molecule must be larger. (25) R. regenerated from the hydrochloride by use of pyridine. Decomposition products of the ozonide of "Regenerat I" contain laevulinic aldehyde and acid, methyl-cyclohexanone, diacetylpropane, undecatriene, trisemiacarbazone and pentadecatriene.
- Harries, C. & Evers, F. (1) Reduction of R. dihydrochloride in ethylene dichloride by Zn dust. Large yield of alphahydrocactouc. Light yellow powder, m.p. 120-130° C. m.w. in bromoform.  $C_{20}H_{32}$  or  $C_{20}H_{30}$ . Formula  $(CH_2-C(CH_3)=CH-CH_2)_8$ .
- Harries, C. & Fonrobert, E. (1) R. regenerated from its hydrochloride by pyridine. (3) Vulc. R. gives 2 hydrochlorides of R. One is soluble in  $CHCl_3$  and the other one containing S is insoluble. After treating the hydrochloride with pyridine the product cures poorly. There has been a shift of the double bonds, and the ozonide yields diacetylpropane on hydrolysis along with laevulinic acid and laevulinic aldehyde. This shift does not occur in the vulc. process.
- Heinzerling, C. (1) p. 29. Conc. HCl and HCl gas slowly change R.
- Hinrichsen, F. W. & Memmler, K. (1) p. 50. Description of C. O. Weber's method of preparing Dihydrochloride of R. Heated to 40° C., HCl splits off leaving a mono-hydrochloride which is stable at 130° C.
- Hinrichsen, F. W., Quensell, H. & Kind-scher, E. (1) When dried gaseous hydrogen halide was passed into a cooled solution of R. in  $C_6H_6$  or  $CHCl_3$ , a dihydrochloride ( $C_{10}H_{16} \cdot 2HCl$ ), a dihydrobromide and a monohydroiodide ( $C_{10}H_{16}HI$ ) was obtained. Alcoholic NaOH does not completely remove the halogen. See Chlorine.
- Lichtenberg, O. (1) Derivatives and thermal dissociation of R. hydrohalides. R. regenerated from the ozonide reacts with HCl and Br. Action of HCl on R. regenerated from the ozonide.
- Matthews, R. (1) Aqueous HCl has no effect on R.
- Obach, E. F. A. (1) No appreciable action on gutta percha.
- Ostromuiskenskii, I. (18) Vulc. of R. by heating with the halides or hydrohalides of R. (26) Vulc. of R. by the hydrochloride of R.
- Peachey, S. J. (6).
- Ramsay, W. (1) Gutta percha is rendered tougher and harder by heating under pressure at 180° C. or 200° C. for 12 hrs. with 5% HCl.
- Roxborough, W. (1) HCl does not affect R.
- Seeligmann, Torrillon & Falconnet. (1) p. 132. Conc. HCl and HCl gas slowly change R.
- Siemens & Halske. (1) See Chlorine. (2) Reduction of R. hydrochloride by Zn dust.
- Stevens, H. P. (30) See Sulfuric Acid.
- Tassilly, E. (1) p. 313.
- Thomson, W. & Lewis, F. (1) HCl,  $HNO_3$ ,  $H_2SO_4$ ,  $H_2CrO_4$ , citric and tartaric acids on R. Only the first three have important action.
- Weber, C. O. (14) Prepared the addition product of HCl and R. ( $C_{10}H_{15}Cl_2$ ).
- Hydrocyanic Acid.**
- Kerbosch, M. (4) Found in Hevea Latex.
- deVries, O. (24) p. 188. Inhibits coagulation.
- Hydrofluoric acid.** See Latex-Coagulants.
- Frank, F. & Marekwald, E. (5) R. from the Cameroon was improved in color and freed from mold by use of Purub.
- Traun, H. (2) HF containers made from a mixture of R. and paraffin. May be vulcanized.
- Berthelot. (1) See Hydriodic Acid.

- Gorter, K. (10) See Ageing-Oxidation.  
 Griesheim-Elcktron. (1) See Regeneration.  
 Harries, C. (13) Unsuccessful in reduction of R. by H<sub>2</sub>. (31) Reduction of R.  
 Hinrichsen, F. W. & Kempf, R. (1) Hydrogen is not added to R. in the presence of platinum black.  
 Lascelles-Scott, W. (16) (17) Action of H<sub>2</sub> on R. as generated from a copper-zinc couple.  
 Pummerer, R. (1) The double bonds of R. are not reacted upon by hydrogen and palladium. Perhydrocaoutchouc has high mol. wt., is soluble in ether, swells in solvents and is elastic.  
 Pummerer, R. & Burkhard, P. A. (1) Hydrogenation of R. at room temp. and at 80° C. in the presence of platinum. Product is (C<sub>2</sub>H<sub>10</sub>)<sub>n</sub>. Oxidation of R. hydrocaoutchouc by oxygen and perbenzoic acid.  
 Staudinger, H. & Fritsch, J. (1) H<sub>2</sub> on purified R. at 270° C. and 100 atmosphere pressure in presence of platinum. Complete hydrogenation. Ni is not satisfactory. The product is (C<sub>2</sub>H<sub>10</sub>)<sub>n</sub>, does not add bromine, is colloidal but non-elastic, soluble in C<sub>6</sub>H<sub>6</sub>, etc., insoluble in acetone, etc. Unattacked by vulcanizing agents showing vulc. to be addition at double bonds. Heat distillation of R. gave isoprene, dipentene and hydrocarbons, C<sub>15</sub>H<sub>24</sub>, C<sub>20</sub>H<sub>32</sub> and C<sub>25</sub>H<sub>40</sub>. Distillation of hydrocaoutchouc gives (C<sub>2</sub>H<sub>10</sub>)<sub>n</sub> the lowest being pentane, the highest C<sub>50</sub>H<sub>100</sub>.  
 Venable, C. S. & Fuwa, T. (1) Solubility of H<sub>2</sub> in R.
- Hydrogen.**  
 Anon. (270) Hydrogen has been combined with R. to produce an effect similar to that of S.  
 Austerweil, G. (1) Loss of H<sub>2</sub> through deteriorated R. may be due to diffusion. Good R. also shows loss of H<sub>2</sub> not by diffusion but by absorption and subsequent osmosis.
- Hydrogenation.** See Hydrogen.
- Hydrogen peroxide.**  
 Boswell, M. C. (1) See Ageing-Oxidation.
- Fickendey, E. (1) Raw R. immersed in H<sub>2</sub>O<sub>2</sub> in sunlight became tacky, but not in the dark. See Ageing-Tackiness.  
 Hampe, W. (1) Action on gutta percha.  
 Kirchhof, F. (1) H<sub>2</sub>O<sub>2</sub> on raw R. produces tackiness. A peroxide was recognized in the washed product.  
 Koechlin, H. (1) R. passes over into a soluble modification on treatment with H<sub>2</sub>O<sub>2</sub>. This R. solution colors wool yellow, on evaporation, due to oxidation of sulfur compounds in the wool. Reducing agents prevent this.  
 Lascelles-Scott, W. (8) H<sub>2</sub>O<sub>2</sub> has deleterious action on R.  
 Ostromuiskii, I. (11) Proposed as a vulc. agent of R.  
 Terry, H. L. (3) Action on R.  
 Thomson, W. & Lewis, F. (1) Dilute solution has no effect on cold vulc. R.  
 Weber, C. O. (3) Oxidation of R. by H<sub>2</sub>O<sub>2</sub> proceeds slowly. Oxidation was incomplete after 3 weeks treatment with an ethereal solution containing 32 volumes available oxygen.
- Hydrogen Persulfides.**  
 Bloch, I. (1) H<sub>2</sub>S<sub>2</sub> or H<sub>2</sub>S<sub>3</sub> for vulc. of R. in solution.  
 Bourquin, H. (1) Described work of Bloch (1).  
 Bruni, G. & Romani, E. (1) Unable to duplicate Bloch (1).  
 Scott, W. & Bedford, C. W. (1).  
 Stevens, H. P. (46).  
 Walton, J. H. & Parsons, L. B. (1) Properties and preparation.
- Hydrogen Sulfide.** See Peachey Process.  
 Ahrens, F. (6) The loss of total S of vulc. R. on ageing is probably due to loss as H<sub>2</sub>S.  
 Anon. (178) Mercury oxychloride, lead chromate, zinc chromate and lead colors are blackened by H<sub>2</sub>S when used in R.  
 Bell, P. C. (1) H<sub>2</sub>S liberated during vulc. had often been noted prior to the year 1894.  
 Blanc, M. le & Kröger, M. (1) Vulc. of R. solutions by iodine and H<sub>2</sub>S.  
 Burghardt, C. A. (1) Vulc. consists in the alteration of the caoutchouc through production in it of a sulfo compound. A certain amount of hydrogen of the caoutchouc being replaced by S.

- Bysow, B. V. (3) R. and S heated to 160° C. The temp. rises quickly to 225° C. and H<sub>2</sub>S is given off. See Vulcanization-Theories.
- Caspari, W. A. (1) H<sub>2</sub>S is evolved in the vulc. of gutta percha and balata. See Balata.
- Dubosc, A. (7) See Whale Oil. (13). (23) See Starch, and Vulcanization-Theories. (30) Org. accels. react with S to produce H<sub>2</sub>S. Metallic oxides and S give sulfur dioxide. The two gases then unite to form active S. Resins, crude petroleum, waxes, bitumens, tannins and turpentine are weak accels. since they generate H<sub>2</sub>S during vulc. See Sulfur Dioxide and Vulcanization-Theories. (40) Any organic material which will react with S or CS<sub>2</sub> to form H<sub>2</sub>S or sulfoeyanic acid can be considered as a vulc. accel. Sawdust, bran, starch and other forms of cellulose are included in this class. See Vulcanization-Theories.
- Itersen, G. van. (1) H<sub>2</sub>S noted in ebonite cures.
- Kimishima, T. (1) See Thioaniline.
- Pahl, W. (1) Some H<sub>2</sub>S is formed during vulc. with S which either diffuses out or is retained.
- Payen, M. (3) R. can absorb a volume of H<sub>2</sub>S almost equal to that of its own.
- Peachey, S. J. (34) Data on proportions, methods, etc., of vulc. by H<sub>2</sub>S and SO<sub>2</sub>.
- Perkin, F. M. (1) Vulc. is an addition process of S because H<sub>2</sub>S is not evolved.
- Potts, H. E. (4) S adds on to R. with the evolution of H<sub>2</sub>S.
- Romani, E. (3) See Furfural.
- Scott, W. & Bedford, C. W. (1) The accelerating action of organic bases is explained by the formation of their hydrosulfides which form polysulfides similar to ammonium polysulfide.
- Schidrowitz, P. (8) Vulc. is not accompanied by the evolution of any appreciable quantity of H<sub>2</sub>S.
- Seidl, E. (1) Only compounds which give off H<sub>2</sub>S induce a reaction between PbO and S.
- Stevens, H. P. (73) H<sub>2</sub>S is not evolved during vulc. A trace is formed by action of S on resins and proteins.
- Terry, H. L. (3) Vulc. is a substitution process accompanied by H<sub>2</sub>S evolution.
- Tilche, E. (1) R. is vulc. in an atmosphere of H<sub>2</sub>S and NH<sub>3</sub>.
- Venable, C. S. & Fuwa, T. (1) Solubility in R.
- Weber, C. O. (2) R. vulcanized with S on a small or large scale gives no trace of H<sub>2</sub>S. (10) No evolution of H<sub>2</sub>S was noted during vulc. of R. with S. (13) See Vulcanization. (61) The "insoluble constituent" of R. slowly combines with S under vulcanizing conditions to form H<sub>2</sub>S.
- Whitby, G. S. (1) H<sub>2</sub>S inhibits coagulation.
- Hydrogen Sulfide and Sulfur dioxide.**  
See Peachey Process.
- Hydroquinone.**  
Bayer & Co. (41) See Ageing-Tackiness.
- Heilbronner, A. (1) See Tannin.
- Kratz, G. D., Flower, A. H. & Coolidge, C. (1) Retards the vulc. of R. twice as much as phenol. See Aniline.
- Moureaux, C. & Dufraisse, C. (1) See Ageing-Oxidation.
- Hydro-Salicylamine.**  
Dubosc, A. (54) An accel.
- Hydrosulfites.**  
Heilbronner, A. (1).
- Hydroxylamine.** See Aldehyde-Amines.
- 8-Hydroxyquinoline.**  
Spoon, W. (1) See Quinisol.
- Hypochlorous Acid.**
- Hypochlorites.** See Calcium Hypochlorite.
- Editorial. (3) Description and chemistry of vulc. by hypochlorites.
- Claubry, H. G. de. (1) Calcium hypochlorite and S for vulc. of R.
- Gottlob, K. O. (6) p. 97. Hypochlorites used to vulc. R.
- Marckwald, E. & Frank, F. (4) & (11) Hypochlorites will vulcanize R. to an ebonite.
- Marzahn, R. (1) p. 466-7. Na and Ca hypochlorites have a vulc. action on R.

- Ostromuiskii, I. (15) Vulc. of R. by the free acid or by its Ca or Na salts to a horny product.
- Porritt, B. D. (1) p. 40. HOCl or hypochlorites have been used to vulc. R. in the cold. (2) Notes on materials used in the R. industry.
- Zsigmondy, R. & Spear, E. B. (1) p. 257. HOCl or hypochlorites used to vulc. R. in the cold.

**Hyposulfites.****"Black Hypo."****"Burnt Hypo."****"Eureka Compound."** See Zinc or Lead hyposulfites.

Anon. (68) See Sulfur-Bloom.

Camille, A. (22) "Burnt hypo" preferred to flowers of S since the resulting compound is less harsh.

Jennings, J. G. &amp; Lavatier, M.L.J. (1) Vulc. of R. without free S.

Marcy, E. E. (2) Vulc. with Pb and Zn hyposulfites in combination with their sulfides.

Moulton, S. (1) &amp; (2) Vulc. with Pb and Zn hyposulfites in combination with their sulfides.

Pearson, H. C. (1) p. 64. Lead hyposulfite is a mixture of sulfide and free S.

Pickles, S. S. (4) Vulc. of R. in absence of free S.

Trotter, J. D. (1) Vulc. of R. with zinc hyposulfite.

**Imido - tetramethyl - diamido - diphenyl - methane.** See Auramine O.**Indigo.**

Lascelles-Scott, W. (35) White indigo prevents perishing or oxidation of natural and vulc. R. See Latex-Preservatives. (36) Indigo slows up the rate of oxidation of R. in ozone. Gamboge, a gum resin, preserves raw and vulc. R. slightly. Gamboge and leuco indigo together in R. slow up rate of oxidation more than the leuco indigo alone.

**Inosite.****Inositol.** See Methyl Inositol.**Iodine.** See Bromine and Chlorine.

Baudrimont. (1) Action of varying amounts of I in KI on vulc. R.

Pure KI has no action. Unvulcanized R. is not attacked by I in KI. Pure I in KI in alcohol does not alter vulc. R. without water present. The change is due to I acting on S. Since the liquid iodide solution attacks R. in presence of calcium carbonate the change is not due to acid developed.

Baumetz, M. (1) Action of I on R.

Blanc, M. le & Kröger, M. (1) Vulc. of R. solutions by iodine and H<sub>2</sub>S. See Viscosity.

Blossom, T. M. (1) Action of halogens on R. See J. B. Newbrough &amp; E. Fagan (1) (2) (3) &amp; (4).

Bolas, T. (1) Warren vulc. insulated wire with iodine.

Boswell, M. C. (1) See Ageing-Oxidation.

Camille, A. (20) Dental vulcanite was made by J. B. Newbrough and E. Fagan with their I and Br process. S was also used. Vapors of Cl, Br and I may be used like S<sub>2</sub>Cl<sub>2</sub>.

Caspari, W. A. (1) Iodine acts on gutta percha, balata and R. The products darken at 180° C., very little I given off below 200° C.

Degen &amp; Kuth. (1) Vulc. of R. solutions with I.

Dubosc, A. & Luttringer, A. (1) p. 171. C. O. Weber prepared the iodide of R. by the action of I on a CS<sub>2</sub> solution of R. Prior to that time I was thought to have no action on R.

Eduardoff, F. (1) Action of I on R. resins. (2) Action of I on fresh latex.

Gladstone, J. H. & Hibbert, W. (1) Iodine has little or no action on R. in CHCl<sub>3</sub>.

Gottlob, K. O. (6) p. 6 &amp; 71.

Herbst, E. &amp; Stern, R. (1).

Hinrichsen, F. W. & Kempf, R. (1) Reaction of R. and I is more rapid in sunlight, but is not accelerated by ultraviolet light. R. gives C<sub>20</sub>H<sub>20</sub>O<sub>4</sub>I<sub>2</sub> in atmosphere of I.

Hinrichsen, F. W. &amp; Memmler, K. (1) p. 50.

Koninck, D. &amp; Lejeune. (1) Iodine is removed from a potassium iodide solution by R.

Marckwald, E. &amp; Frank, F. (11) 25-30% bromiodide at 120° C. used in England in 1870 for production of hard R.

- Newbrough, J. B. (1) Tungsten oxide used with I to prevent vulc. during mixing.
- Newbrough, J. B. & Fagan, E. (1) Iodine is combined with R. prior to vulc. S may or may not be used. (3) Iodine and S are heated independently in turpentine, the solutions are mixed and added to R. The R. is vulc. by heat. (4) Vulc. of R. by incorporation of I or Br and the application of heat. S may be used. Turpentine may be treated with S or  $\text{H}_2\text{SO}_4$  and used as a solvent for the halogens.
- Parkes, A. (1) Vulc. with vapors of iodine.
- Paulet, F. (1) Vulc. is assisted by adding I to R. mixes after the other pigments. Any desired color in finished article can be made.
- Pearson, H. C. (1) p. 67.
- Porritt, B. D. (2).
- Scherpe, H. (1) Vulc. of R. solutions with I.
- Seeligmann, Torrilhon & Falconnet. (1) p. 132 & 163. Acts on R. like S but more energetically.
- Warren, T. T. P. B. (1) Vulc. of R. for cable covers by dipping in solutions of halogens. S not used. I or Br may be added directly to the R. before applying to the cable. Finished wire is baked to remove excess halogen. R. so treated is more easily vulc. by S than raw R.
- Weber, C. O. (4) By the addition of I to R. and S it may be vulc. in a shorter time at  $115^\circ \text{C}$ . than with S alone. Iodine forms sulfur iodide, which vulcanizes R. and liberates the iodine which acts as a catalyst. See Antimony Iodide. (10) Bromine and iodine addition products of R. are known, the corresponding acid is not liberated. (14) Iodine derivative of R. (61) p. 36.  $\text{C}_{10}\text{H}_{16}\text{I}_2$  prepared.
- Iron Dithiocarbamates.** See Dithiocarbamates.
- Molony, S. B. & Nikaido, Y. (1) (2).
- Iron Oxide.**
- Anon. (161) Iron oxide has a harmful effect on R.
- Bell, P. C. (5) Causes deterioration of R.
- Breuil, P. (10) Hydrated iron oxides are indifferent to R. Cold vulc. ( $\text{S}_2\text{Cl}_2$ ) articles containing iron oxide are easily oxidized but not when hot vulcanized. Iron oxide diminishes resilience.
- Ditmar, R. (33) 3-8% used as an accel. in R. with a high content of factis. (62) An accel. of vulc.
- Dubosc, A. (7) An accel.
- King, A. H. (1).
- Weber, C. O. (5) Ferric oxide if dry can be used in R. goods, otherwise basic ferric chlorides form during vulc. which cause deterioration of R. (27) Iron oxide in cold curing of R. with  $\text{S}_2\text{Cl}_2$  causes formation of iron chloride which has a deteriorating action on R.
- Iron Sulfide.**
- Lascelles-Scott, W. (26) Iron proto-sulfide and R. exert a mutual protective action.
- Warnes. (1) Iron sulfide used in manufacture of steam joints and also for its vulcanizing properties.
- Iron Xanthates.**
- Cadwell, S. M. (4) (5) & (6) See Xanthates.
- Iso-amylamine.** See Amylamine.
- Iso-butylaldehyde.** See Aldehyde-Amines.
- Iso-nitroso camphor.**
- Ostromuiskii, I. (15) Will not vulc. a mix of R. and PbO as do the nitro compounds.
- Isoprene.** See Distillation of rubber.
- Barrows, F. E. (1) The reactions of isoprene.
- Bouchardat, G. (3) HCl on isoprene gives a mono- and dichlorhydrate and a product which has the properties and elasticity of R. On dry distillation of the latter material the same volatile hydrocarbons are obtained as with R. This material, a polymer of isoprene, seems to be identical with R.
- Bruin, G. de. (1) Crystalline addition compound of  $\text{SO}_2$  and isoprene.
- Euler, W. (1) & (2) Constitution of isoprene.



- Harries, C. (29) Action of ozone on isoprene.
- Ipatiew, W. (1) Constitution and synthesis of isoprene.
- Ipatiew, W. & Wittorf, N. (1) Obtained by dry distillation of R.
- Mokievsky, W. (1) HOCl on isoprene gave two compounds,  $C_8H_{11}ClO$  b.p.  $141^\circ C$ . and  $C_8H_{10}Cl_2O$  b.p.  $81^\circ C$ .
- Tilden, W. A. (1) Constitution of isoprene and its formation from terpenes. (2) Isoprene with HCl polymerizes to a tough elastic solid. Isoprene spontaneously changed to R. on standing. This is accounted for by assuming that a small amount of acetic or formic acids formed by oxidizing action of the air caused this transformation.
- Wallach, O. (1) Isoprene at  $260^\circ C$ . gives Kautschin ( $C_{10}H_{16}$ ) b.p.  $180^\circ C$ . Kautschin adds bromine to give  $C_{10}H_{16}Br_4$  m.p.  $125.6^\circ C$ ., and HCl to give  $C_{10}H_{16} \cdot 2HCl$  m.p.  $49.50^\circ C$ . (2) Suggests that isoprene bromide with  $NH_3$  may give pyridine derivatives. The products are basic.
- Williams, C. G. (1) Isolated isoprene and Kautschin from dry distillation of R.
- Isopropyl Alcohol.**
- Ostromuiskenskii, I. (13) A weak accel. in the presence of metallic oxides.
- Jelutong.**
- Alexander, P. (2) Resin of Jelutong R. contains a compound ( $C_{20}H_{40}O$ ), m.p.  $161^\circ C$ .
- Cohen, N. H. (1) Lupeol acetate and alpha and beta amyrin acetate are found in Jelutong resin.
- Hillen, G. H. (1).
- Hinrichsen, F. W. & Marcusson, J. (1) Jelutong resin is not an oxidation product of  $C_{10}H_{16}$  but more probably an alcohol of the cholesterol series.
- Kautchin.** See Caoutchin, Caoutschen, Caoutchecine.
- Anon. (168).
- Himly, F. C. (1) In fraction of distillate boiling at  $140^\circ$  to  $280^\circ C$ . This compound gives halogen, hydrochloric acid and oxygen derivatives.
- Wallach, O. (1) See Isoprene.
- Williams, C. G. (1).
- Kautschin.**
- Bouchardat, G. & Lafont, J. (1) Kautschin and acetic acid give a monoacetate. Hydrochloric acid converts it into a dichlorhydrate, and alcoholic KOH into a monohydrate. m.p.  $25^\circ C$ .
- Kautschukin.**
- Birchall, F. W. (2) Kautschukin rapidly absorbs oxygen, changing to a resinous mass which resembles shellac. S oxidizes kautschukin. Oxidation of the latter is the cause for hardening and brittleness of R. goods.
- Kerm's mineral.**
- A mixture of antimony trisulfide and trioxide. See Antimony Sulfides.
- Ketooxalates.**
- Badische Co. (1) See Ageing-Oxidation.
- Laevulinic Acid.** See Laevulinic Aldehyde.
- Harries, C. (6) R. ozonide hydrolyzes to ketoaldehydes, dialdehydes and  $H_2O$ . The latter oxidizes the aldehydes to acids. Isolated laevulinic acid. (9) R. ozonide breaks down to laevulinic aldehyde, aldehyde-peroxide and acid. (11) 5 g. R. ozonide,  $C_8H_{10}O_4$ , gives 2.3 g. laevulinic aldehyde and 1-1.5 g. laevulinic acid. 5 g. Gutta percha ozonide gives 1 g. aldehyde and 3 g. acid. (13). (20) Relative amounts of acid and aldehyde from R. Diozonide vs Diozonide. (22) Decomposition of ozonides from regenerated R. (25) See Rubber-Hydrochloride. (29) From isoprene R. (31) p. 57.
- Steimmig, G. (1) See Laevulinic Aldehyde.
- Laevulinic Aldehyde.** See Laevulinic Acid.
- Bayer & Co. (17) (18) See Ozone.
- Bruni, G. (4) R. in oxygen at  $77^\circ C$ . for 10 days shows test for laevulinic aldehyde.
- Fonrobert, E. & Harries, C. (1) p. 154. Laevulinic aldehydes by hydrolysis of R. ozonides.
- Gorter, K. (7) Found in tacky R.
- Harries, C. (25) See Rubber-Hydrochloride. (27) Further data regard-

- ing the work of G. Steimmig (1). (29) 46% from Elberfeld isoprene R. (31) p. 56.
- Kaye, F. (7) Present in aged R. goods.
- Luff, B. D. W. (2) Review.
- Steimmig, G. (1) Laevulinic acid and aldehyde, succinic acid and acetylonyl acetone from synth. R.
- Whitby, G. S. (12) Formation from oxidized R.
- Laevulinic Diperoxide.**
- Fonrobert, E. & Harries, C. (1) p. 153. Harries, C. (10). (23).
- Lamp Black.** See Carbon, Gas Black.
- Bradley, W. P. (1) See Ageing-Oxidation.
- Marckwald, E. & Frank, F. (12) American gas black gives higher tensile strength and elongation than German lamp blacks but the latter give higher elasticity or resilience. Microscopical examination.
- Williams, H. J. (1) pt. V. Manufacture of lamp black and bone black.
- lanolin.** See Cholesterin.
- Latex.**
- Allen. (1) Latex and its analysis.
- Anon. (64) See Colloid Chemistry of Rubber. (99) Composition and properties. (101) Hevea latex globules have an average diam. of 3.5 micromillimeters. 50 million globules per c.c. Dilution with 20% NaCl stops the Brownian movement. (126) Latex contains phosphates and sulfates with small amounts of chlorides and oxalates of K, Ca, Mg, and Fe. Nitrogenous substances classed as protein and gluco-proteins. Acetaldehyde also present. (150) See Variability. (228) C. O. Weber prepared a R. from *Castilloa* latex as pure or better than the best Para R.
- Arens, P. (1) See Ageing-Oxidation. (5) Collection and preparation of latex.
- Arisz, W. H. & van Vlissingen, L. R. E. S. (1) Influence of heavy tapping on chemical composition of latex. Amount of resin remained constant. Organic substances in serum decreased, while inorganic remained constant.
- Bamber, M. K. (3) Latex or coagulum heated above 70° C. to render oxidase inactive and thus prevent oxidation.
- Barrowman, A. T. (1) Hevea latex behaves as an emulsion rather than as a suspension. The caoutchouc globules are liquid and not solid. Viscosity of latex at various dilutions.
- Beadle, C. & Stevens, H. P. (12) Analysis for proteins, acetone extract, ash and R. in Hevea latex. (13) Hevea latex is higher in protein than other latices. Half the protein is retained in the coagulum. (17) Latex is an emulsion of R. and resins. In actual solution are potash salts, sugars, l-methyl inositol and nitrogenous substances.
- Biffen, R. H. (1) Hevea latex is slightly alkaline and contains R-32%, proteins 2.3%, Ca and Na salts-9.7%, traces of resin and water.
- Bobilioff, W. Jr. (1) Globules of Hevea latex vary from 0.5 $\mu$  to 3 $\mu$ . They are smallest in new leaves and shoots. Latex in new shoots independent of that in the rest of the tree. Latex is formed in lactiferous tissue itself.
- Bois, E. du. (1) Collection and coagulation of latex. Viscosity and polymerization.
- Campbell, L. E. (5) Creaming of latex is thickening of latex in early stage of coagulation without loss of fluidity. Flocking of latex is formation of small particles without coalescence of the same to form lumps.
- Cayla, V. (2) Experiments point to presence of a rennet-like enzyme in R. latex.
- Christy, C. (1) Coagulation of *Fun-tumia Elastica*. Slow methods: Spontaneous, HCHO and alcoholic creosote. Rapid methods: Boiling, mercuric chloride, tannic acid and heat, alum and heat, plant juices and heat. Acetic acid useless as a coagulant. R. prepared by tannic acid or mercuric chloride deteriorates rapidly. Formol R. is strong and resists oxidation.
- Crossley, W. (2) Colloids of Hevea latex adsorb acids, a part of which

- is so firmly retained by the R. as to affect its physical properties.
- Davidson, S. C. (7) Salts which precipitate S by action of acids are added to latex prior to coagulation.  $K_2S_3$ ,  $Na_2S_2O_3$ ,  $CaS_2$ . (8) Freshly coagulated R. is treated with  $K_2S_3$  solution to remove traces of acid and to precipitate S in the R.
- Denier & Vernet, G. (1) "Dambosite" only bacterium found in Hevea latex which attacks sugars and produces acids. (2) 27 species of bacteria have been isolated of which one attacks sugars, while others decompose proteins or liquefy gelatine.
- van Dillen, L. R. (1) Sugars in Hevea latex.
- Eaton, B. J. (6) Exudation of serum causes "rustiness" on sheet R. Prevented by washing in water before drying. (9).
- Esenbeck, N. v. & Marquart, E. (1) Latex from leaves does not contain R. Composition of *Ficus Elastica* Latex and nature of the resin content.
- Fickendey, E. (2) Peptones play an active part in coagulation of Funtumia latex because dialysis and formalin cause coagulation. Proteins and peptones act as protective colloids. (3) Small size of *Kickxia Elastica* particles  $0.5\mu$  to  $1\mu$  one reason for difficult coagulation of latex, the other is presence of peptones. Metaphosphoric acid best precipitant.
- Flamant, G. (1) Two proteins from latex of Funtumia Elastica and Landolphia Owariensis. One similar to albumin and one like vegetable caseins. Reagents precipitating both proteins will coagulate the latex at once. Reagents precipitating but one of the proteins give incomplete coagulation. See Colloid Chemistry of Rubber.
- Fourcroy, A. (2) Analyzed latex of Hevea Guyanensis. Acids coagulate and alkalis do not. R. soluble in turpentine and ether. Fourcroy considered the absorption of oxygen the main cause of the separation and solidification of the R. Presence of proteins not mentioned (1791).
- Frank, F. (9) See Protein. Peptones play an active part in coagulation of Funtumia latex.
- Frank, F., Gnaedinger, J. & Marckwald, E. (1) Studies on *Kickxia* latex. West African rubbers contain balsamic resins while East African contain harder resins. The serum contained dextrorotatory proteins probably glyco-proteins. Cinnamic acid present. Presence of rhamnose and phlobaphene indicated.
- Frank, F. & Marckwald, E. (4) The protective bodies hindering coagulation in *Kickxia* latex may be glucosidic, glyco-proteins or glyco-peptones. Method of coagulation and not origin determines quality of R. High protein content not good for high quality. Vulc. tests.
- Gassicourt, Cadet de. (1) Weak mineral acids coagulate latex, conc. acids slowly decompose it.  $HNO_3$  colored the solution yellow. Sugar present in latex (1825).
- Geer, W. C. (5) p. 5 & 63. White milk from the bark of certain trees was noted by Columbus. The Spaniards observed the natives playing with balls of coagulated latex.
- Girard, A. (1) Isolated a sugar like substance in R. latex called Dambonite. (2) R. globules all of same size as fat globules in animal milk. Any reagent added to milk for coagulation must be used in conjunction with heat.
- Gnädinger, J. (1) A study of the constituents of the serum water of *Kickxia* latex. In coagulation all water soluble proteins should be removed and those of high molecular weight should not be attacked by coagulants.  $Al_2O_3$  decomposes protein bodies in R. and prevents harmful action of the products formed. Nature and composition of R. resins.  $Al_2O_3$  added to R. causes the resin content to remain constant and the R. is not affected by the resins.
- Gorter, K. (5) *Castilleja* latex contains chlorogenic acid. *Ficus Elastica* latex contains chlorogenic acid and a magnesium salt of tetrahydroxy adipic acid which was shown to be alpha-saccharic acid.
- Henke, G. (1) Study of the latex of various euphorbiaceae.

- Henri, V. (2) R. globules have diameter of  $0.5\mu$  to  $2.0\mu$ . Acids and salts of di- and trivalent metals are most active coagulating agents of latex. (4) Agglutination as brought about by alkalies, salts of di- or trivalent metals is reversible. Coagulation as caused by acids not reversible. (6) Study of Brownian Movement of latex and effect of alkalies, acids and other reagents on it.
- Jacobson, F. (1) See Resins.
- Jong, A. W. K. de & Tromp de Haas, W. R. (1) Found proteins, tannin, an acid ( $C_{10}H_{20}O_{10}$ ),  $CaCl_2$ , sugar and a compound giving a green color in neutral solution in latex of *Castilloa Elastica*.
- Jumelle, H. (1) Latex from branches contains resins but no R.
- Kaye, F. (3) Phosphorous content of Hevea latex varies considerably.
- Kerbosch, M. (4) Acetone was not found in Hevea latex. Proved presence of HCN. (6) Acetaldehyde and hydrocyanic acid found in steam distillate of Hevea latex.
- Koller, P. (1) See Ammonia.
- Lascelles-Scott, W. (1) Isolation of resins, albumin and sugar from latex.
- Lewton-Brain, L. (1) The more concentrated the latex the more rapid the cure. Retention of moisture during first few days aids in decomposition of the protein. Review of Eaton & Grantham.
- Lock, R. H. & Bamber, M. K. (1) Variation of percent of R. in latex.
- Marckwald, E. & Frank, F. (6) p. 41. Nitric acid precipitates a white amorphous compound from aqueous portion of latex which is identical with Faraday's albumin.
- Morris, D. (1) Latex is a complex fluid containing caoutchouc, proteins and resins.
- Moureaux, C. & Dufraisse, C. (1) See Ageing-Oxidation.
- Netherlands Government Institute. (1) 15% of the dry material of latex is composed of non-caoutchouc compounds. Analysis.
- Pettigout, E. (1) Chemistry and coagulation of latex. Chemical and physical properties of R. HF has no action on R. while conc. HCl,  $H_2SO_4$  and  $HNO_3$  attack it.
- Seeligmann, Torrilhon & Falconnet. (1) Properties of latex.
- Semler, H. (1) Proteins in R. latex.
- Spence, D. (5) No pentoses found in dialysate of *Funtumia Elastica* latex. K present and traces of magnesium. No iron or calcium in dialysate, they are therefore present in an insoluble form in latex. *Funtumia R.* contains no potassium, therefore the washing process is efficient. (10) Analysis of *Ficus Vogelii* latex. High percent of magnesium and absence of phosphates, characteristic of this latex. (13) *Funtumia* globules much smaller ( $0.5\mu$ ) than Hevea globules which are  $2\mu$ . The former is harder to coagulate.
- Spoon, W. (2) Latex from dormant trees. (5) Quebrachitol and sugar in latex.
- Stevens, H. P. (13) See Methyl Inositol. (39). (73) Globular size of R. in latex. (74) Recent developments of the plantation R. industry.
- Tromp de Haas, W. R. (1) Effect of tapping on the composition of the latex.
- Ultee, A. J. (17) Stearic acid in latex of *Ficus Fuvla*.
- Ure, A. (1) 2 samples of latex examined. No coagulation with alcohol. Not miscible with caoutchoucine or naphtha. Insol. in soda lye.  $HNO_3$  gives a red curdy magma.
- Vernet, G. (1) Latex is an emulsion of R. globules in an aqueous solution of proteins, resins, sugars, diastases, organic acids and different mineral salts. Properties of crude R. depend on method of coagulation. Resin and protein content varies as the method of coagulation.
- Vesterberg, K. (1) Amyrine, a mixture of triterpenic isomeric alcohols,  $C_{30}H_{50}OH$ , found in latex of a large number of plants.
- de Vries, O. (8) The heavier the tapping the higher the sp. gr. of latex and more rapid the cure and higher the viscosity of the R. (18) Heavy tapping causes decrease of R. content, rate of cure decreases, tensile strength remains the same. (24) p. 10. Composition of latex. The serum contains an accel. of vulc. p. 24. See Starch.

Weber, C. O. (25) Composition and coagulation of Castilloa *Elastica* latex. (50) R. contained in latex as a liquid surrounded by albuminous covering. On bursting this covering the contents polymerize to a solid mass.

Weil, R. (1) Colloid chemistry of rubber.

Whitby, G. S. (1) Changes in latex due to enzymes, oxidases or anaerobic and aerobic decomposition. (7) Bacteria that may act on both carbohydrates and proteins, preferentially act on the former; thus explaining why addition of sugars prevents decomposition of nitrogenous constituents of latex. Putrefactive activity in latex produces an anti-coagulating effect quite apart from that caused by the alkalinity developed.

Zsigmondy, R. & Spear, E. B. (1) Chemistry of latex. Theory of coagulation and vulcanization.

#### **Latex-Acidity of.**

Beadle, C. & Stevens, H. P. (13) Fresh latex is occasionally alkaline.

Biffen, R. H. (1) Hevea latex is slightly alkaline.

Bobilioff, W. Sr. (1) Reaction of latex to litmus was more or less acid and sometimes neutral.

Henri, V. (1) Hevea latex is faintly alkaline.

Kaye, F. (3) Acidity of latex before and after coagulation. Standardization of coagulation.

Morgan, S. (1) p. 215. Latex has an acid reaction.

Parkin, J. (8) Alkalinity could never be detected with red litmus.

Preyer, A. (1) Latex of *Ficus Elastica* is neutral when fresh.

Romburgh, P. van. (3) Latex is slightly acid.

Ultee, A. J. & Dillen, L. R. van. (1) Acidity of latex increases on standing due to bacterial decomposition. Acidity may be depressed with soda.

Ultee, A. J. & Spoon, W. (1) Acidity of latex.

de Vries, O. (24) p. 24. Fresh Hevea latex is nearly neutral.

Whitby, G. S. (1) Fresh latex is faintly alkaline but within one half hour it is faintly acid.

**Latex-Coagulation.** See Variability.

Anon. (249) Coagulation depends on the precipitation of the proteins in the latex. (266) Acetic acid most suitable coagulant. Excess does no harm. Excess of formic, lactic, sulfuric and hydrofluoric acids retards cure. Spontaneously coagulated R. cures faster than when coagulated with acids. Machining freshly coagulated R. lengthens time of cure. Papain did not remove an appreciable amount of protein when added to latex but R. cured faster than when coagulated with acetic acid.

Barritt, N. W. (1) Conc. of salts in latex bears an important relation to coagulation of latex and on the strength of the vulc. R. NaCl produces coagulation. Range within which no coagulation occurs decreases with increasing amounts of salt.

Barrowcliff, M. (1) Natural coagulation due to enzyme action. Acid coagulation also brought about by enzyme action. Natural coagulation complete in 10-12 hrs. in absence of air, in air incomplete in 2 to 3 days because CO<sub>2</sub> prevents development of alkali by putrefactive bacteria. Theory of latex coagulation.

Beadle, C. & Stevens, H. P. (13) Found no gap for H<sub>2</sub>SO<sub>4</sub>, so that it may be used over a greater range than acetic acid. After dialysis latex reacts normal to coagulation, so that crystalloids play no part in coagulation. Nature of coagulation. Microscopic studies. Use of CaCl<sub>2</sub>, acetic acid, HCl and H<sub>2</sub>SO<sub>4</sub>. (18) coagulation methods made necessary by the world war.

Bellerio, L. (1) Coagulation in an alkaline medium.

Biffen, R. H. (1) Hevea latex coagulated by centrifuging. The R. is free from odor and is less liable to decomposition. Latex coagulated with smoke from dry distillation of uricuri nuts. Smoke contains acetic acid and creosote. Latter prevents decomposition of proteins in latex.

Bolas, T. (2) Preparation of R.

Boutaric, J. (2) Preparation of R.

Cayla, V. (4) Chemical action of smoke. (8) Causes of Variability of

- Brazilian and Plantation rubbers. Preparation. Maintenance of quality in Brazilian R.
- Chaplet, A. (1) Review of coagulation of latex, composition of R., its properties and reactions, deresination, etc.
- Crossley, W. (2) No evidence of any chemical action between acetic acid and any constituent of latex. Coagulation due to physical causes. Latex behaves towards chemical reagents like other colloidal suspensions. Precipitation of protein not sufficient explanation of coagulation of R.
- Davidson, S. C. (3) A soluble salt of sulfur, such as liver of sulfur added to latex, which on acidifying will decompose and precipitate nascent S. HCHO or alkalized cresote may also be added. Suitable coagulants are,  $\text{H}_2\text{SO}_4$ , HCl, HF and trichloroacetic acid.
- Dekker, P. (3) Résumé of coagulation methods.
- Ditmar, R. (47) Discussion of methods of coagulation and the use of various coagulants. (48) Theoretical on effect of size of agglomerates in coagulated R. (49) Constituents and coagulation of latex.
- Eaton, B. J. (3) Amount of coagulant, dilution, age of latex and oxidases. (25) Denier & Vernet isolated a bacteria capable of coagulating latex. Enzyme theory is still unproven. Inhibiting effect of  $\text{K}_2\text{CrO}_4$  or NaI may be because they are bactericides while accelerating action of calcium salts may be due to action on the living organisms by favoring those responsible for natural coagulation at the expense of others which inhibit coagulation.
- Eaton, B. J. & Whitby, G. S. (1) Pyroligneous acid from distillation of wood, used as coagulant. Rate of cure of sheet and slab, but not of crepe was retarded. Pure phenol added to latex retards rate of cure of sheet but not of slab. Smoking has preserving action but slows up rate of cure.
- Eduardoff, F. (2) Solid caoutchouc added to latex causes instantaneous coagulation of certain African latices and to a greater or less degree with Hevea, Kickxia and Manihot.
- Flamant, G. (1) Rôle of proteins in coagulation of Funtumia and Londolphia latices.
- Frank, F. (9) Funtumia latex contains peptones and is not affected by acids but by HCHO, tannin, etc. All protein precipitants also coagulate R. Ca, Mg and alkali salts are found in R. and phosphoric, sulfuric and oxalic acids are present in latex. The coagulant should leave these salts soluble so that they do not act injuriously on the R. For this reason Parub is a good coagulant.  $\text{H}_2\text{CO}_3$  separates the inorganic bases as indifferent salts in the R. A slowly coagulated R. does not have as good quality as a rapidly coagulated one.  $\text{CaCl}_2$  a good coagulant. Fe, Mn, Cu, & Hg salts should not be used as coagulants. Alum should not be used. A good method of coagulating Funtumia and Ficus latices is by spraying into boiling water. Bacterial changes are reduced to a minimum by removal of the proteins.
- Gardner, H. C. T. (1) Coagulation is a physical phenomenon. Pellicule surrounding R. is not protein, since R. is still subject to coagulation after its removal. Coagulation by acids may be produced by decomposition of resin particles forming pellicules around the globules thus producing a negative surface tension.
- Gassicourt, C. de. (1).
- General Rubber Co. (3) A stabilized R. coagulum, coagulated under the pressure of its coagulation-expansion. Bacterial action prevented by 0.2% beta naphthol, 0.1% NaF, 0.5% pine tar cresote in sodium cresylate or 0.1% Hexa. (6) Latex treated with an enzyme, coagulase, adapted to coagulate the latex. Vulc. agents may also be added to latex before coagulation. (8) Latex coagulated in presence of Hevea seed pulp. Composition comprising an admixture of R. and Hevea seed pulp.
- Gortler, K. & Swart, N. L. (2) Coagulation results from the action of microorganisms and is favored by presence of sugars. Sugar undergoes fermentation forming acids which cause coagulation. Excess sugar inhibits fermentation.

- Hart, J. H. (1) (2) Nature of coagulation.
- Heim, F. (2) Coagulation without acid.
- Heim, F. & Henriect. (1) Mechanism of coagulation.
- Heim, F. & Marquis, R. (1) Resins play active part in coagulation of Landolphia.
- Henri, V. (1) Coagulation effected by mixtures of alcohol with very small amounts of bivalent salts or acids, while alkalis have an inhibitory effect. There is a gradual transition from agglutination to coagulation. (1) (4) Experiments on dialyzed latex. Monovalent metals and alcohol have no effect. Ca, Mg, & Ba cause coagulation. Mn, Ni, Co, Cu, Zn, Pb, & Al produce agglutination when present in concentrations of 0.05 N. Acids produce a clot at 0.5 N. Acetone clots the latex. A feeble coagulant produces flocculation and an energetic one a single clot. Structure of the clot and tensile strength of dry clot vary with nature and concentration of the coagulant. (2) Mechanism of coagulation. (3) Alkalies cause flocculation of latex. With neutral or acid solutions, salts of di- or triatomic metals, alcohol and acetone the latex coagulated in hard elastic lumps. Tendency to coagulation much stronger with acids. (5) Salts of bivalent or trivalent metals added to alkaline solution of latex results in agglutination. The separated material may be suspended in the liquid again by shaking. (6) Method of coagulation has influence on properties of the R. Heat produces tackiness in uncured samples. Comparison of strength of R. prepared in various ways.
- Henry, Y. & Ammann, P. (1) *Funtumia Elastica* latex, HCHO, heat or vegetable juices are used as coagulants.
- Höhncl, F. v. (1) Classification of R. as to method of preparation. Use of alum, brine or acid as coagulants.
- Hubener, G. (11) Review of researches on latex and latex coagulation.
- Jong, A. W. K. de. (1) Coagulation of *Castilloa* latex is retarded by presence of an albuminous material. It is precipitated by alcohol and acetone and not by acetic acid. Found the calcium salt of tannic acid, an acid  $(C_{17}H_{30}O_{10})_x$ . KCl, and sugar (osazone m.p. 200° C.) in the latex.
- Jumelle, H. (1) Effect of various coagulants and anti-coagulants on the vulcanizing properties of the R. (2) Influence of method of preparation of R. on vulc.
- Kaye, F. (3) Standardization of coagulation. Effect of coagulants on yield of R. and the acetone extract.
- Kerckhove, G. von den. (2) Coagulation of *Landolphia* vine latex.
- Lascelles-Scott, W. (1) In general any free acid, acid salt or saline solution will coagulate latex. Alum gives an inferior R. Nearly all acids or acid salts are injurious to R. HCl is preferred.
- Lecompte, H. (1) Mercuric chloride does not coagulate *Landolphia* Hendelotti. Amount of alcohols required for coagulation varies as their mol. wt. Oxidase observed in *Hevea*, *Castilloa* and *Manihot* latex.
- Lindet, L. (2) Lindet's work on casein analogous to Vernet (5) on R. CaCl<sub>2</sub> precipitates the phosphate and citrate salts along with the coagulum.
- Marckwald, E. (1) Preparation of Plantation R. Review.
- Marckwald, E. & Frank, F. (10) Coagulation of *Manihot* latex with various coagulants. Ca and Mg phosphates give remarkably good results.
- Parkin, J. (2) Coagulation due to separation of protein from the latex by the coagulant.
- Pearson, H. C. (1) p. 44. Description of coagulation methods. Soap, astringent juices, salts and tannin.
- Preyer, A. (1) *Ficus Elastica* coagulates with alcohol or by boiling with or without acids. Alkalies hinder coagulation. Each globule of R. surrounded by a coating of protein. Hot formic acid tried as coagulant. (4) Preparation of R. by drying, heating, chemical and spontaneous coagulation from leaves of different trees. Latex of leaves contains a substance capable of inducing coagulation.
- Schidrowitz, P. (9) Theories of coagulation.

- Schidrowitz, P. & Kaye, F. (1) Comparison of twelve methods of coagulation. R. coagulated by water has a high resin content.
- Schulte, A. (2) See Formaldehyde.
- Spence, D. (33) Ammonia,  $\text{Na}_2\text{CO}_3$  or  $\text{NaOH}$  retard coagulation.  $\text{NH}_4\text{Cl}$ ,  $\text{CaCl}_2$  and  $\text{BaCl}_2$  only hasten coagulation on heating. Acids in small amount favor coagulation but an excess has a retarding effect. Alcohol hastens coagulation.
- Spence, D. & Russel, W. F. (2) Kickia latex coagulated by formalin or tannin. The rubber cured slower than Hevea but was of high grade.
- Stevens, H. P. (63) Fractional precipitation of latex. The first fraction contains the bulk of the R. and vulcanizes more rapidly.
- Thomas & Maude. (1) Coagulation without use of preservatives or coagulants has been patented.
- Torrilhon, L. (1) Summary of known processes of coagulation.
- Ure, A. (1) Coagulation of latex by boiling.
- Vernet, G. (2) Coagulation by evaporation, heat, acids and salts. Heating in hot water at  $80^\circ\text{C}$  prevents darkening of R. Amazonian process vs. acetic acid coagulation. (3) Coagulation results from "insolubilization" of proteins. Desiccation and centrifuging do not effect coagulation. Assumption of existence of bacteria unnecessary to explain coagulation. Latex below  $4^\circ\text{C}$  will not coagulate. (6)  $\text{CaCl}_2$  accelerates coagulation of Hevea latex and increases yield of R. Calcium phosphate formed is incorporated with the R.
- de Vries, O. (24) p. 138. A study of creaming, flocking, clotting and coagulation. Creaming of latex obtained in castilloa latices but rarely in Hevea latex.
- de Vries, O. & Hellendoorn, H. J. (4) Latex coagulated by heat gives of low viscosity and increased tensile strength are unaltered.
- de Vries, O. & Spoon, W. (1) Coagulation of the Ilcken-Do coagulation.
- Weber, C. O. (25) Fresh
- Elastica latex cannot be coagulated by heat. A glucoside of dambonite found in the latex. List of coagulants given.
- Whitby, G. S. (1) The gap in which no coagulation occurs is very distinct for  $\text{HCl}$  and  $\text{HNO}_3$  and indistinct for  $\text{H}_2\text{SO}_4$ ; with large amounts of acetic acid no coagulation takes place. A coagulating enzyme will coagulate latex. Anaerobic decomposition of protein in parts of R. not exposed to air. Aerobic decomposition sets in at surface. Hevease, an oxidase, produces discoloration. Oxygenase not detected in fresh latex.
- Whitby, G. S. (5) Large amounts of acids work as protein precipitants, whereas the action of small amounts of acid is due to intermediation of enzymes. Comparison of coagulation of latex and clotting of milk. Effect of calcium salts on coagulation. Bactericides such as toluene and thymol that are harmless to enzymes do not inhibit natural coagulation, while  $\text{HCN}$  or  $\text{KCN}$ , which paralyze enzymes, prevent coagulation.
- Zimmerman, A. (3) Coagulation of Manihot R. Sunlight causes tackiness.
- Latex-Coagulants-Acetic Acid.**
- Baervelt, J. F. (1) Coagulation by gases obtained by destructive distillation of wood after removal of tar.
- Beadle, C. & Stevens, H. P. (13) See Latex-Coagulation.
- Byrne, F. A. (1) Latex coagulated & uncoagulated subjected to produced by volatilizing rived from destructive wood wast
- Chevalier  
latex



- (19) Acetic acid most suitable coagulant. Alum and  $\text{H}_2\text{SO}_4$  are not recommended.
- Magen, A. A. (1) Hevea latex coagulated by residues obtained by distillation of wood in a closed vessel.
- Parkin, J. (1) Introduced as a latex coagulant in Ceylon in 1898-99. An excess has deleterious effect on R. Strong solutions give a faster drying R. (4) Acetic acid coagulation. (8) The range over which good coagulation occurs with acetic acid is greater than with other acids.
- Schidrowitz, P. (4) Amount of acetic acid bears little if any relation to quality of R. Too little acid gives coalescence, while too much gives hard and brittle rubbers.
- Schidrowitz, P. & Goldsbrough, H. A. (2) Observations on acetic acid coagulation.
- Spence, D. (14) See Formic Acid.
- Stevens, H. P. (23) Increase of acid in coagulation gives slower curing R. (38) Acetic acid from acetylene as a coagulant. (57) Smoked Sheet prepared by use of pyroligneous acid prepared from coconut shells, gave satisfactory vulc. tests. (65) Increase in amount of acetic acid used has greater effect on rate of combination with S than on physical properties. The effect is directly proportional to the retardation of combination of R. and S. Alum retards less than  $\text{H}_2\text{SO}_4$  and is preferable to it. (70) Slab R. from acetic acid coagulation tested in ZnO and PbO mixes. (77) Coagulation with acetic acid in 1922.
- (9).  
     Rate of cure decreases  
     of acid but  
     the same.  
     Amount of  
     yellow  
     and
- deVries, O. & Spoon, W. (3) Spontaneous vs. acetic acid coagulation.
- Whitby, G. S. (1) With large amounts of acetic acid no coagulation takes place. See Latex-Coagulation.
- Latex-Coagulants-Alcohol.**
- Clarkson, Wm. (1) Coagulation, cleaning and antisepticizing of latex by a solution of alcohol, water and aldehyde.
- Ilcken, C. A. & Down, St. V. B. (2) Treatment of latex with absolute ethyl alcohol or mixed with methyl alcohol and petroleum benzine in liquid or gaseous form to coagulate R.
- Jong, A. W. K. de. (1) Castilloa latex is coagulated by alcohol and acetone and not by acetic acid.
- Lecompte, H. (1) The amount of alcohols required for coagulation varies as their mol. wt.
- Livingston, G. B. & Cairney, W. D. (1) Latex poured into coagulant which is a mixture of alcohol and an aldehyde.
- Preyer, A. (1) Ficus *Elastica* latex coagulates with alcohol.
- Rankin, R. (1) Coagulation with alcohol.
- deVries, O. (22) Comparison of various latex coagulants.
- Latex-Coagulants-Aldehydes.**
- Byrne, F. A. (2) Coagulation with  $\text{HCHO}$ , acetaldehyde or acrolein.
- Eichelbaum, G. (2) Aldehyde sulfoxalates used to coagulate latex.
- Fulton, R. C. & MacCallum, D. A. (1) Coagulation with aldehydes other than  $\text{HCHO}$ .
- Henry, Y. & Ammann, P. (1)  $\text{HCHO}$  as coagulant for *Funtumia Elastica*.
- Livingston, G. B. & Cairney, W. D. (1) Coagulation with acetaldehyde.
- Spence, D. & Russel, W. F. (2) Kickxia latex coagulated with  $\text{HCHO}$ . See Latex-Coagulation.
- Latex-Coagulants-Alum.**
- P. (5) Not recommended because precipitates nitrogenous matter giving lower yield of R. R. is short and brittle.
- Alum as a coagulant for latex gives a rubber inferior to para R.

- Eaton, B. J. (9) Retards the cure. (20) & (21) Retards the cure and is not recommended. (23) & (26) Emphasizes the injurious effect of alum used as a coagulant. (25) Alum is deleterious to R.
- Lascelles-Scott, W. (1) Alum gives an inferior R.
- Pearson, H. C. (1) p. 48. Used for coagulating wild R.
- Schlessinger, (1) Latex coagulated with alum.
- Schmidt, E. A. (2) Good coagulant for *Castilloa* latex. Acetic acid and formalin are not.
- Spoon, W. (2) Alum as a coagulant. (3) As a coagulant it yields a poor grade of R.
- Stevens, H. P. (40) In absence of Na sulfite it gives a slow curing rubber. (70) Effect of alum on slab R. when tested in ZnO and PbO mixes. See Sulfur-Coefficient of Vule.
- deVries, O. (22) Comparison of various coagulants for latex. (24) p. 181. One of the oldest known coagulants—harmful to inner properties of R., retards cure of smoked sheet and crepe.
- Weber, C. O. (36) Alum forms an insoluble product with proteins of latex. R. of poor quality is obtained.
- Latex-Coagulants-Carbon Dioxide.**
- Esch, W. (15) CO<sub>2</sub> is a valuable coagulant because it evaporates. Use of mineral and citric acids should be abandoned. The serum and residue of coagulating agents should be thoroughly removed.
- Flamant, G. (1) Coagulation of French Congo latex with CO<sub>2</sub> at 55° C.
- Pahl, W. (2) CO<sub>2</sub> which contains vapors of aqueous HCl passed into latex at 30° C. CO<sub>2</sub> may be mixed with acetic or formic acids. (3) Coagulation with smoke and CO<sub>2</sub>.
- Ripeau, F. (1) Coagulation with CO<sub>2</sub>. Effect of agitation during coagulation.
- Latex-Coagulants-Formic Acid.**
- Anon. (262) No influence on tensile strength and chemical composition of rubber. An excess retards rate of cure.
- Byrne, F. A. (1) Vapors obtained by heating formic acid may be used for coagulation and/or curing of R.
- Eaton, B. J. (9) See Latex-Coagulants-Acetic Acid.
- Eaton, B. J., Grantham, J. & Day, F. W. F. (1) No difference in rate of cure between formic and acetic acids used to make sheet or crepe rubber.
- Gorter, K. & Swart, N. L. (1) More active coagulant than acetic acid.
- Morgan, S. (1) p. 218. Gives rubber of same quality as acetic acid.
- Preyer, A. (1) Hot formic acid as coagulant for *Ficus Elastica* latex.
- Spence, D. (14) Properties of rubber coagulated with formic acid as good as when coagulated with acetic acid. Weight for weight formic acid coagulates twice as much rubber as acetic acid.
- de Vries, O. (22) Comparison of various coagulants for latex. (24) p. 179. Stronger coagulant than acetic acid; increase of acid retards cure faster than acetic acid; prevents oxidation to a greater degree than acetic acid.
- Weber, C. O. (62) Formic acid as a coagulant.
- Latex-Coagulants-Hydrochloric Acid.**
- Beadle, C. & Stevens, H. P. (13) See Latex-Coagulation.
- Davidson, S. C. (3) See Latex-Coagulation.
- Eaton, B. J. (3) Limits of complete and incomplete coagulation with HCl. (9) HF, H<sub>2</sub>SO<sub>4</sub>, and HCl as coagulants give slower curing rubbers.
- Eaton, B. J., Grantham, J. & Day, F. W. F. (1) Mineral acids used as coagulants retard rate of cure. HF has the least and HCl the most effect although not comparable to alum in this respect.
- Lascelles-Scott, W. (1) HCl preferred as a coagulant. See Latex-Coagulation.
- Morgan, S. (1) p. 216 & 233. Used as a coagulant decreases the rate of cure.
- de Vries, O. (22) Comparison of various coagulants for latex. (24) p. 184. Strong latex coagulant but effective within a smaller range than other acids.

Whitby, G. S. (1) Effect of varying amounts of HCl as a coagulant. See Latex-Coagulation.

#### **Latex-Coagulants-Hydrofluoric Acid.**

Cayla, V. (5) "Purub" as a coagulant.  
Eaton, B. J. (9) HF, H<sub>2</sub>SO<sub>4</sub> and HCl as coagulants give slower curing rubbers.

Eaton, B. J., Grantham, J. & Day, F. W. F. (1) Mineral acids as coagulants retard rate of cure. HF has least and HCl the most effect although not comparable to alum in this respect.

Frank, F. (2) R. coagulated with HF vulcanizes so rapidly that S is in complete combination with R. before it combines with any PbO in the mix.

Morgan, S. (1) p. 216 & 224. Purub does not give a superior R.

Sandmann, D. (1) R. coagulated with HF or its salts is vulc. to ebonite with S and PbO without formation of appreciable amounts of PbS. HF or fluosilicic acid, alkali chlorides, etc. used as coagulants. (2) Rubbers coagulated with Purub aged better in 1½ years than those prepared with acetic acid. Purub stops putrefaction. Fermentation of sugars is not stopped.

de Vries, O. (24) p. 184. Use of HF as a coagulant.

Zimmerman, A. (2) NaF as a coagulant for latex of *Manihot Glaziovii*. (3) (5).

#### **Latex-Coagulants-Hydrofluosilic Acid.**

Edwardes, J. (1) Coagulation with hydrofluosilic acid or its salts. The acid or salt retards oxidation and prevents mold formation.

Sandmann, D. (1) HF or fluosilicic acid, alkali fluorides, etc., used to coagulate R.

#### **Latex-Coagulants-Lactic Acid.**

Anon. (265) When used as a coagulant gives a R. similar to that obtained with acetic acid.

Boehringer & Sons. (1) Al lactate and acetate as coagulants.

Spoon, W. (2) Al lactate and lactic acid as coagulants. (3) R. prepared with Al lactate shows reduced tensiles and slower rate of cure. Type

of R. is similar to that obtained with alum.

de Vries, O. & Spoon, W. (4) Lactic acid retards rate of cure. Other properties are unchanged.

#### **Latex-Coagulants-Miscellaneous.**

Anon. (83) Fruit juices and fermented coconut water as coagulants. (88) Papain (Papaw Sap) is twice as powerful a coagulant as acetic acid. R. has normal rate of cure and tensile strength but dries slowly. (288) Purub-HF, Martinol-Wood distillate containing acetic acid, methyl alcohol and phenolic compounds. Pracol-alum. "Compound"-Mixture of acetic and cresylic acids.

Beadle, C. & Stevens, H. P. (13) Use of CaCl<sub>2</sub>, Acetic acid, HCl and H<sub>2</sub>SO<sub>4</sub>. Ether coagulates *Castilloa Elastica* latex.

Collins, A. E. (1) Hevea latex: Acetic acid, formic acid, lime juice, sulfuric acid. *Castilloa* latex-NaHCO<sub>3</sub> and lime juice aid in rising of cream. NaHCO<sub>3</sub> gives greenish color to R. and diminishes resin content.

Davidson, S. C. (3) See Latex-Coagulation.

Eaton, B. J. (9) Tartaric acid a suitable but not economical coagulant. Oxalic and citric acid as coagulants. See Latex-Coagulants-Acetic Acid. (23) Alum is injurious to R. when used as a coagulant. Starch has no effect on rate of cure. Boric, tannic, molybdic and phosphotungstic acids all have retarding effect when using 1-2%.

Eaton, B. J., Grantham, J. & Day, F. W. F. (1) Citric acid gives a R. having same vulcanizing properties as when acetic acid is used as a coagulant.

Eduardoff, F. (2) Use of cresol, Koa-latex, phenol, acetic acid and alcohols as coagulants.

Foureroy, A. F. & Nicholson, W. (1) Coagulation by O<sub>2</sub>, heat, alcohol and HNO<sub>3</sub>.

Gibson, W. T. (1) H<sub>3</sub>PO<sub>4</sub> as a coagulant for *Kickxia* latex.

Lascelles-Scott, W. (2) Tartaric, citric and oxalic acids coagulate latex and preserve the R. Potassium quadrox-

- alate, tannic and acetic acids are good coagulants.
- Leonard, W. A. (1) Fermented coconut milk coagulates R. as well as acids. No effect on nerve or ageing of the R.
- Lindet, L. (1) Girard, A., found that heating to 30° C was sufficient to cause R. globules to rise to surface and unite. Alum, NaCl, H<sub>2</sub>SO<sub>4</sub>, lemon juice and 4% phenol solution containing H<sub>2</sub>SO<sub>4</sub> give good coagulation.
- Marx, T. (1) Coagulation of Manihot glaziovii with sea water, acetic acid, phenol, lime and CaCl<sub>2</sub>, MgCl<sub>2</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, ZnSO<sub>4</sub>, formic acid and phenol, and aniline chlorhydrate solution.
- Morgan, S. (1) p. 215. Comparison of coagulants.
- Pahl, W. (3) Coagulation by smoke and CO<sub>2</sub>.
- Parkin, J. (5) NaCl does not coagulate dilute latex.
- Ripeau, F. (1) Coagulation by smoke.
- Smith, J. G. & Bradford. (1) Coagulation by acetic, sulphuric or trichloroacetic acids, NaCl, heat, evaporation, churning, and centrifugalizing. NH<sub>3</sub> retards coagulation. (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> gives a very pure R. by precipitating proteins which are liable to decomposition. Formalin gives a high quality R. and prevents decomposition.
- Stevens, H. P. (65) Increase of amount of coagulant has greater retarding effect on rate of cure in sheet than crepe R. Alum is less satisfactory than acetic acid and H<sub>2</sub>SO<sub>4</sub> less satisfactory than the others.
- Ultee, H. J. (10) Coagulated latex in both acid and alkaline medium by use of papain.
- de Vries, O. (22) Discusses the action of the following coagulants: SO<sub>2</sub>, alum, wood-vinegar, fermented coconut water, acid coffee bean juice, Spiritus, formic, lactic and hydrochloric acids. (24) p. 188. Sodium bisulfite as a coagulant resembles H<sub>2</sub>SO<sub>4</sub> in its effect on the qualities of the R.
- de Vries, O. & Hellendoorn, H. J. (8) Large amount of HCl retards rate of cure, not as much as H<sub>2</sub>SO<sub>4</sub>. Tensile strength and viscosity decreased.
- Weber, C. O. (36) Since coagulation of latex is due to coagulation of albumins the following are suggested as latex coagulants, hydroferrieyanic, tungstic and gallic acids.
- Zimmerman, A. (5) Coagulation with HF, HCl, HNO<sub>3</sub>, Oxalic acid, Br water, H<sub>2</sub>O<sub>2</sub>, CaCl<sub>2</sub> and NaHSO<sub>4</sub>.
- Latex-Coagulants-Salts.**
- Anon. (86) 5% NaHSO<sub>4</sub> precipitates 20% of R. from latex. The R. is of very high quality.
- Beadie, C. & Stevens, H. P. (13) CaCl<sub>2</sub> as latex coagulant. See Latex-Coagulation.
- Colloseus, H. (1) Coagulation with water-glass, borax, Na<sub>2</sub>PO<sub>4</sub>, CaCl<sub>2</sub> and other salts. Latex diluted with alkali and coagulated by salts and oxides of alkaline earth metals, i.e. MgO, etc. (2) An alkali or equivalent water soluble salt added to latex. Coagulation is then obtained by adding alkaline earth or heavy metal salts. Free acid of R. is removed and less decomposition takes place.
- Lindet, L. (2) CaCl<sub>2</sub> as a coagulant. See Latex-Coagulation.
- Marekwal, E. & Frank, F. (10) Ca and Mg phosphates give good results as coagulants for Manihot latex.
- Mosinger, E. (2) Coagulation of latex by Al, Bi or Zn chloride or mixtures of these salts.
- Pearson, H. (1) NaCl used in coagulation of vine latex of French Congo. This R. became sticky.
- Spoon, W. (2) CaCl<sub>2</sub> as a coagulant for latex.
- Vernet, G. (1) CaCl<sub>2</sub> accelerates coagulation.
- de Vries, O. (24) p. 189. NaCl used as a coagulant decreases rate of cure and viscosity of the R. The R. dries very slowly.
- Zimmerman, A. (3) CaCl<sub>2</sub> an efficient coagulant for latex of Manihot Glaziovii. BaCl<sub>2</sub>, MgCl<sub>2</sub> and MgSO<sub>4</sub> do not give as good results as CaCl<sub>2</sub>.
- Latex-Coagulants-Sodium Sulfate.**
- Barritt, N. W. (1) Influence of Na<sub>2</sub>SO<sub>4</sub> on coagulation with H<sub>2</sub>SO<sub>4</sub> and acetic acid.

- de Vries, O. (24) p. 102 & 188. Less effect as coagulant than  $\text{NaHSO}_4$ . No influence on properties of the R.  
 Whitby, G. S. (1) Hot solutions of  $\text{Na}_2\text{SO}_4$  produce a floccy precipitate.

#### **Latex-Coagulation-Spontaneous.**

- Anon. (262) & (264) Spontaneously coagulated R. is as good as acetic acid coagulated R. and rate of cure is faster.  
 Barrowcliff, M. (1) Function of acid in ordinary coagulation is to accelerate action of enzymes. (2) R. coagulated in closed vessels without acids. No putrefaction occurs. Calcium acetate or sulfate accelerate coagulation. Coagulum does not darken. Known as M. C. T. process by M. Maude & W. S. Crosse.  
 Campbell, L. E. (2) Natural coagulation is due to enzymes. It is retarded by heat, neutral salts, alkalies and formalin. Natural clotting of Hevea latex aided by  $\text{CaCl}_2$ . Natural clotting retarded or inhibited by heating, neutral or faintly acid potassium oxalate, sodium fluoride, alkali and formalin.  
 Cayla, V. (1) See Enzymes. (3) Mentions a coagulating enzyme in fresh latex of *Ficus elastica*.  
 Denier & Vernet, G. (2) Sugar accelerates anaerobic coagulation. Darkening of R. prevented by absence of air or use of antiseptics.  
 Eaton, B. J. (19) Latex under anaerobic conditions coagulates in 12-18 hrs. at  $30^\circ \text{C}$ . Addition of sugar is an aid to coagulation. Latex frozen 6-8 hrs. coagulates on thawing.  
 Henry, Y. & Anmann, P. (1) *Funaria elastica* latex has tendency to spontaneous coagulation.  $\text{HCHO}$ , heat and vegetable juices will coagulate the R.  
 Parkin, J. (2) Assumed bacterial action in spontaneous coagulation.  
 Spence, D. (15) First noted the action of enzymes in spontaneous coagulation.  
 Spoon, W. (2) Complete coagulation of latex in closed vessel with 0.05% to 0.10%  $\text{CaCl}_2$ . (4) Spontaneous vs. acetic acid coagulation.  
 Stevens, H. P. (19)  $\text{CO}_2$  generated in spontaneous coagulation prevents putrefaction. Enzyme action appears to be primary cause of coagulation although enough lactic acid develops to carry out coagulation in regular manner.  
 Vernet, G. (3) Spontaneous coagulation obtained by adding sugar and excluding air and keeping at  $30^\circ\text{--}45^\circ \text{C}$ . See Latex-Coagulation. (5) Evidence advanced to support Eaton & Grantham's theory that spontaneous coagulation is due to presence of microorganisms in latex.  
 deVries, O. (24) p. 159 & 200. Methods of spontaneous coagulation. Spontaneous coagulation forms lactic and succinic acids. p. 204. Anaerobic coagulation gives a white R. Rate of cure is faster.  
 deVries, O. & Spoon, W. (3) Spontaneous vs. acetic acid coagulation.  
 Whitby, G. S. (1) Anaerobic natural coagulation prevents putrefaction and coagulation proceeds normally. (5) Spontaneous coagulation is due to presence of specific enzyme in latex. (8) p. 50. Natural coagulation not due to an oxidase but to enzyme action.

#### **Latex-Coagulants-Sugar.**

- Chevalier, M. A. (1) Coagulation of latex with acetic acid vs. sugar.  
 Denier & Vernet, G. (1). (2) Accelerates anaerobic coagulation.  
 Eaton, B. J. (4) Sugars promote natural coagulation. (11) Sugar aids coagulation by bacterial formation of lactic acid together with small amounts of acetic and succinic acids. Absence of air favors lactic acid formation.  
 Eaton, B. J. & Grantham, J. (7) Medium for anaerobic bacteria is provided for coagulation of R. latex by adding dextrose, sucrose, lactose, arabinose, mannose, laevulose.  
 Girard, E. & Rose, E. (1) Glucose and sucrose may replace acetic acid for coagulating Hevea latex.  
 Gorter, K. & Swart, N. L. (1) Sugars promote natural coagulation.  
 Spoon, W. (2) Use as coagulant for latex. (4) Use as a coagulant for latex.  
 Stevens, H. P. (4) Coagulation with a saccharated solution of lime.

Ultee, A. J. (6) Sugar as a coagulant.  
Vernet, G. (2) Coag. of latex with sugar. R. is not injured. (5) Large amounts of sugar inhibit coagulation.  
deVries, O. (7) Uniformity of R. with sugar coagulation equals acetic acid process. R. has good keeping quality. (24) Coag. with sugar.

#### Latex-Coagulants-Sulfur Dioxide.

Berry, A. E. & Boake, A. (1) 5% solution of  $\text{SO}_2$  produces immediate coagulation and inhibits oxidation, darkening and bacterial action.

Byrne, F. A. (3) Coagulation by  $\text{SO}_2$  gas.

Lintner & Co. (1) Latex coagulated by gaseous or a solution of  $\text{SO}_2$ .

Morgan, S. (1) p. 225. The limits within which good coagulation can be obtained with  $\text{H}_2\text{SO}_3$  are narrow.

deVries, O. (15)  $\text{H}_2\text{SO}_3$  has favorable influence on inner qualities of the R. compared with acetic acid. Rate of cure is unchanged, tensile strength and viscosity of R. are increased. (24) p. 102 & 186. Prevents surface oxidation and darkening of R. No effect on rate of cure. Rate of drying is decreased.

#### Latex-Coagulants-Sulfuric Acid.

Beadle, C. & Stevens, H. P. (13) See Latex-Coagulation.

Davidson, S. C. (1) Coagulation with  $\text{H}_2\text{SO}_4$ ,  $\text{MgSO}_4$  or pyroligneous acid. (3) See Latex-Coagulation.

Eaton, B. J. (9) HF,  $\text{H}_2\text{SO}_4$  and HCl as coagulants give slower curing rubbers. (14) "Coagulatex" consists of 50%  $\text{H}_2\text{SO}_4$  with some HCl and mineral salts. Not recommended due to harmful action of  $\text{H}_2\text{SO}_4$ . (25)  $\text{H}_2\text{SO}_4$  and  $\text{NaHSO}_4$  as coagulants give inferior R. (28) "Acidotex" is principally  $\text{H}_2\text{SO}_4$  which is deleterious to Hevea latex.

Frank, F. & Marekwald, E. (2) R. may be coagulated with  $\text{H}_2\text{SO}_4$  without danger of subsequent tackiness.

Henri, V. (6) Coagulation with  $\text{H}_2\text{SO}_4$  in presence of phenol gives a R. with high tensile strength.

Rousseau, Ph. (1) Coagulation with  $\text{H}_2\text{SO}_4$  and "phenyl saure."

Stevens, H. P. (30)  $\text{H}_2\text{SO}_4$  has a stronger retarding effect than acetic acid. (40)  $\text{H}_2\text{SO}_4$  gives a slower cur-

ing R. than alum. (70) Slab R. from  $\text{H}_2\text{SO}_4$  coagulation tested in  $\text{ZnO}$  and  $\text{PbO}$  mixes.

de Vries, O. (22) Comparison of various coagulants for latex. (24) p. 176.  $\text{H}_2\text{SO}_4$  as a coagulant exerts an antioxidizing action. Decreases rate of cure and viscosity of R. R. coagulated with minimum amount of  $\text{H}_2\text{SO}_4$  ages well.

Whitby, G. S. (1) See Latex-Coagulation.

#### Latex-Coagulants-Tannic Acid.

Lascelles-Scott, W. (2) A good coagulant.

Pearson, H. C. (1) p. 44. Coagulation with tannic acid.

Schulte, A. (1) Coagulation with tannic acid.

Spence, D. & Russel, W. F. (2) Kiekia latex coagulated with tannin.

See Latex-Coagulation.

deVries, O. (24) p. 180. Tannic acid as a coagulant.

#### Latex-Dilution of.

Anon. (266) Dilution before coagulation has no effect on rate of cure. Excessive dilution is deleterious to quality.

Campbell, L. E. (4) Dilution of latex has little effect on rate of cure.

Parkin, J. (5) NaCl does not coagulate dilute latex.

Sharples, A. (1) Dilution of latex or excess of coagulant favor "Spotting" of R.

deVries, O. (24) p. 254. Dilution of latex with water slows up the cure, dilution with serum increases the rate of cure.

#### Latex-Evaporated.

Anon. (123).

Eaton, B. J. (32) Discussion of Hopkinson process. See Natural Accelerators.

General Rubber Co. (12) Latex is pulverized by removing the moisture in a current of hot gases.

Hopkinson, E. (2) Coag. of latex by spraying.

Kerbosch, M. (6) Latex, without coagulation, but preserving all non volatile ingredients is dried in a current of air at  $80^\circ \text{C}$ . and above.

Stevens, H. P. (67) Fast vulc. properties cannot be attributed to putrefactive bases as is the case of matured R. Extracting with water or acetone causes a small decrease in rate of cure or is without effect. Extracting Pale Crepe may increase or decrease the rate of cure. Alkaline slimes on surface of matured R. contain volatile bases when accelerating effect is small.

Zuyderhoff, G. J. (1) Coagulation by evaporation.

#### **Latex-Preexistence of Rubber in.**

Ditmar, R. (8) Insolubility of R. in ether cannot be taken as proof for preexistence of R. in latex. Different latices do not have same chemical composition. (10) Latex is a white, odorless, sweet liquid which takes on the odor of methyl amine in the air. Harries thought pentoses are reduced to  $C_6H_{12}$  which polymerize to rubber. No pentoses were found in latex. Preexistence of R. in latex and function of proteins and sugars in the latex.

Dunstan, W. R. (1) Latex can be coagulated after removal of the proteins. The coagulation is due to polymerization of a fluid in latex from which the solid R. is formed.

Eduardoff, F. (2) R. exists in latex in various degrees of polymerization. Action of I, Br and nitrous gases on latex. Use of Cresol, Koa-latex, phenol, acetic acid and alcohols as coagulants. (3) Latices of different plants contain R. in various states of polymerization. Polymerization is hastened by adding solid R.

Esch, W. & Chwolle, A. (2) Ether dissolves R. Ether extract of latex on evaporation leaves an oil which must still be polymerized. Ordinary R. dissolved in ether leaves the R. unchanged on evaporation. Polymerization of the oil to R. is independent of the presence of proteins.

Hinrichsen, F. W. & Kindscher, E. (3) Mol. wt. of R. is 3173. Caoutchouc is present in latex as such and it is not formed by polymerization during coagulation.

Ostromuiskii, I. (6) Formation of R. in juices of plants.

Stevens, H. P. (44) Review of Harries, C. & Weber, C. O. on nature of R. in latex.

Weber, C. O. (25) R. is formed by polymerization of the oily liquid emulsified in the latex. (48) R. is present in *Castilloa Elastica* as liquid diterpene, in addition there are resins, proteins, an oxidase, Dambonite and a coumarone derivative related to aesculetin. (58) Polymerization ordinarily takes place with loss of double bonds, but R. still has two or more double bonds, therefore its formation is not entirely due to polymerization. Degree of polymerization of R. is very labile and is only stabilized by vulcanization.

#### **Latex-Preservatives.**

Anon. (99)  $NH_3$ , HCHO, potassium oxalate, NaF, creosote, salicylic acid and phenol. (193) The preserving action of  $NH_3$  on latex is increased by use of sandalwood oil, camphor or naphthalene. Creosote will preserve latex but is injurious to R. (262) & (266) No change in tensile strength or composition of R. on adding  $Na_2SO_3$  to the latex. No marked effect on rate of cure. Alkaline creosote solution added to latex has no influence on rate of cure or tensile strength.

Beadle, C. & Stevens, H. P. (13) Behavior of latex preserved with  $NH_3$  and HCHO. Ammonia preserved latex behaves normally toward coagulants after 2-3 days dialysis.

Bilbrough, C. F. S. (1) Phenols and salicylic acid.

Bronner, F. (1) Preservation of R. milk (1852).

Bunker, S. W. (1) Latex preservative consisting of NaOH-90, HCHO-10 and Tetramethylthionin hydrochloride 0.0002, "Anticol."

Campbell, L. E. (3) Creosote and formalin added to latex before coagulation. That part of R. kept moist cured more rapidly than the dry part and contained more resins and proteins. (4)  $Na_2SO_3$  causes no change in tensile strength or composition of R. when added to latex. No effect on rate of cure. Alkaline creosote solution added to latex in first ex-

- periment was without influence on rate of cure but later it was shown that the rate of cure was decreased.
- Cayla, V. (1)  $\text{NH}_3$  on latex of *Ficus Vogelii* causes intense yellow coloration which becomes gray in 24 hours. A microscopic examination showed that only the globules were colored but the solution was clear. (10)  $\text{HCHO}$  prevents coagulation and acts as an antiseptic.
- Chevalier, M. A. (1) Use of  $\text{NaHSO}_3$ .
- Davidson, S. C. (1)  $\text{Na}_2\text{S}_2\text{O}_3$  and "alkalized cresol" added to latex. The  $\text{SO}_2$  evolved on coagulation with acid has a sterilizing and preserving action on R. (2)  $\text{Na}_2\text{S}_2\text{O}_3$  and alkalinized cresol added to latex before coagulation by acid.  $\text{SO}_2$  evolved has a preservative and sterilizing action on the R. (3) Caustic, cresol,  $\text{HCHO}$  and alkaline metallic polysulfides added to latex prior to coagulation by acids. Trichloroacetic, acetic,  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ . (4) Alkalinized cresol, cresylic acid or higher tar acids added to latex prior to coagulation with acid which liberates the preservative substance. Na or K polysulfides may also be present which give free S on acidifying.  $\text{HCHO}$  may also be added. (5) Latex is treated prior to coagulation with an alkaline solution of creosote or phenol either with or without  $\text{HCHO}$ . (6) Latex treated with saponified oleaginous substances and  $\text{HCHO}$  with or without glycerine, creosote or phenol in alkaline solution. A soluble salt of S may also be used. Such treatment prior to coagulation gives a R. of higher purity.
- Day, F. W. F. (1)  $\text{NaHSO}_3$  in latex reduces oxidation.
- Dekker, P. (2) Ammonia preserved latex exhaustively dialyzed did not react normally to coagulants.
- Ditmar, R. (10) Use of guaiacol,  $\text{HCHO}$  and thymol.
- Dubosc, A. (19) Sodium formaldehyde hydrosulfite suggested because of its bleaching, reducing and antiseptic action. (62) Quinosol and potassium oxyquinoline sulfate as disinfectants.
- Eaton, B. J. (3) Boracic acid inhibits coagulation. (26) Formalin,  $\text{NH}_3$ ,  $\text{Na}_2\text{CO}_3$  and other alkaline solutions and  $\text{Na}_2\text{SO}_3$  in dilute solutions. (30) Latex preserved by  $\text{NH}_3$ ,  $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{KCN}$ , Na phenate and soluble fluorides.
- Fourcroy, A. F. & Nicholson, W. (1) Proposal in 1804 to ship latex to France after preservation with caustic.
- Frank, F. (9) Ammonia preserves Hevea and *Ficus latex* but precipitates Funtumia latex.
- General Rubber Co. (1) R. coagulum treated with solution of mono- or polyhydroxy, mono- or polycyclic benzenoids, their esters, salts, polymers or other compounds, such as gallic acid, tannin, cresols, naphthols, diaminophenol, p-aminophenol, to form a semipermeable membrane on the surface and prevent passage of colloidal nitrogenous material. (2) Coagulated or uncoagulated latex treated with an agent, such as betanaphthol, heated at  $80^\circ \text{C}$ . or treated with an enzyme, adapted to insolubilize nitrogenous material and subjected to vacuum evaporation. (3) Bacterial action is prevented by 0.2% beta-naphthol, 0.1%  $\text{NaF}$ , 0.5% pine tar creosote in sodium cresylate or 0.1% Hexa. (5) Process of treating latex with a polycyclic member of the benzene series, betanaphthol, and forming an insoluble substance comprising nitrogenous matter and betanaphthol. (7) Unvulc. R. subjected to vacuo which is then broken by inert gas such as  $\text{CO}_2$ ,  $\text{NH}_3$ ,  $\text{H}_2$  or  $\text{N}_2$ . (9) Latex treated with boric acid which insolubilizes the nitrogenous material, without accelerating coagulation. R. dries rapidly, is free from slime and is not attacked by bacteria. Boric acid may be replaced by salts, esters, polymers or combinations of Boron.
- Hartjens, J. C. (2)  $\text{Na}_2\text{SO}_3$  under certain conditions may increase formation of "spots" on sheet rubber in drying. In such cases soda is preferred as anticoagulant.
- Heurn, F. C. van. (6)  $\text{Na}_2\text{SO}_3$  used to prevent or retard coagulation. Discussion of effect.
- Ilcken, C. A. & Down, St. V. B. (3) Treatment of latices with polyvalent



- alcohols, soluble in water, such as glycerine or glycol or their esters such as triglycerine esters of palmitic and stearic acids, to keep the resins and soluble proteins in solution in the state in which they are present in latex. Coconut oil mentioned. Prevents partial clotting in natural coagulation. (4) Treatment of latices with solution of asphalt prior to coagulation. Treatment of inferior or scrap R. with solution of asphalt.
- Johnson, W. (1)  $\text{NH}_3$  patented as a preservative of latex. (1853).
- Kaye, F. (5)  $\text{NH}_3$  as a latex-preservative.
- Lascelles-Scott, W. (1)  $\text{NH}_3$  prevents coagulation of latex. (2) Effect of insufficient and excess  $\text{NH}_3$  on latex and resultant R. Na phosphate and alkaline cyanides prevent coagulation. Na salicylate and Naphthols are preservatives. Hydronaphthol is used with a minimum amount of  $\text{NH}_3$ . (35) Solution of leuco indigo added to ammonia preserved latex prior to coagulation with  $\text{HCl}$ . 9 months ageing tests show improved resistance to ageing due to leuco indigo.
- Lucas, W. (1)  $\text{NH}_4\text{OH}$  or  $\text{Na}_2\text{CO}_3$  facilitate the flow of latex and retard the formation of lumps.
- McQuire, Ardmore & Coulter. (1) Preservation of latex by sodium phenolate.
- McQuire, Agar, Coulter & Davidson. (1) Preservation of latex by alkalinized phenols.
- Morgan, S. (1)  $\text{Na}_2\text{SO}_3$  has no influence on the properties of the R.
- Morisse, L. P. T. (1) Preservation of latex with  $\text{NH}_3$ .
- Norris, H. L. (1) Preservation of latex (1853).
- Olsson-Seffer, P. (2) S added to latex gives a good R. and preserves it. In smoking process S vapors give a good ageing rubber.
- Parkin, J. (8) Creosote in alcohol added to latex to prevent mold growth. Phenol evaporates too quickly.
- Preyer, A. (1)  $\text{NH}_3$  does not preserve *Castilleja Elastica* latex.
- Schidrowitz, P. & Kaye, F. (2)  $\text{HCHO}$  on latex of *Funtumia Elastica*.
- Schrieke. (1)  $\text{Na}_2\text{SO}_3$  as an anti-coagulant.
- Smith, J. G. & Bradford. (1) Formalin added to latex gives a high quality of R. and prevents decomposition.
- Stevens, H. P. (26) Disinfection of tapping cuts is without effect on the vulcanizing properties of tree scrap. (62)  $\text{NaHSO}_3$  causes slow drying of smoked sheet and retards rate of cure. (71)  $\text{NH}_3$ ,  $\text{NaF}$ , Na silicofluoride and cresols are good preservatives.  $(\text{NH}_4)_2\text{CO}_3$ , pyridine,  $\text{Na}_2\text{CO}_3$ ,  $\text{HCHO}$ ,  $\text{Na}_2\text{SO}_3$ , and phenols or cresols with caustic are unsatisfactory.  $\text{NH}_3$  and caustic are recommended. Data on quantities. (80) Na silicofluoride prevents formation of mold and has no deleterious effect on vulcanizing properties of the R.
- Symington, W. (1) Preservation of R. milk (1853).
- Ultee, A. J. (6) See Sodium Thio-sulfate. (8) Lumps caused by the acid produced by bacteria is prevented by  $\text{HCHO}$  or alkaline substances such as  $\text{NH}_3$ , Soda,  $\text{Na}_2\text{S}_2\text{O}_3$ .  $\text{Na}_2\text{SO}_3$  is recommended.  $\text{Na}_2\text{CO}_3$  good for slow drying sheet. (9) Formalin, quinosol, carbolineum plantarium, crude creoline, Izal, Solignum, Tar,  $\text{Na}_2\text{SO}_3$  and Soda. (15)  $\text{Na}_2\text{SO}_3$  keeps latex as a liquid for 24 hours.
- deVries, O. (15) Soda ranks between  $\text{Na}_2\text{SO}_3$  and formalin as an anti-coagulant. Time of cure slightly decreased.  $\text{NaHSO}_3$  and  $\text{Na}_2\text{SO}_3$  improves the quality of the R.  $\text{Na}_2\text{CO}_3$  in ordinary proportions has very little influence on quality of the R. (15) Anti-coagulants:  $\text{Na}_2\text{SO}_3$ ,  $\text{HCHO}$  and Soda. Antioxidants:  $\text{NaHSO}_3$ ,  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{H}_2\text{SO}_3$  and  $\text{NaC}_2\text{H}_3\text{O}_2$ . (24) p. 82. Anti-coagulants may retard coagulation by neutralizing acids formed in latex or by hindering growth of organisms that produce coagulation. p. 83. Ammonia is the oldest anti-coagulant. Effect of ammonia or ammonium salts formed in coagulation by acids is to retard vulc. p. 85.  $\text{HCHO}$  not equal to  $\text{NH}_3$  for preserving latex. p. 88.  $\text{Na}_2\text{SO}_3$  has favorable effect on prop-

erties of R. but retards the drying of the R. p. 90. Soda acts as an anticoagulant because of its alkalinity. Does not retard drying of R. May cause presence of bubbles due to formation of CO<sub>2</sub>. Very slight effect on qualities of R. p. 91. Formalin, quinosol, creosote, beta-naphthol and boracic acid used to prevent spots caused by bacteria or molds. Following anticoagulants have not been thoroughly studied, borax, boracic acid, NaOH, Na oxalate and Na fluoride. p. 188. HCN inhibits coagulation.

Warren, T. T. P. B. (3) Preservation by NH<sub>3</sub>.

Whitby, G. S. (1) H<sub>2</sub>S inhibits coagulation. (5) HCN or KCN inhibit coagulation. See *Latex-Coagulation*. (8) p. 127. Anticoagulants and their use.

#### Latex-Synthetic.

Alexander, P. (6) Preparation of aqueous R. solutions.

Anon. (34) Emulsifying R. by means of borax solutions. (184) & (213). An 8% solution of R. in borax.

Berzelius, J. J. (1) R. once coagulated cannot again be emulsified.

Camille, A. (14) Borax solutions containing 9-10% of R. (16) Believes that aqueous solutions of R. are possible. (21) Borax water solution of R.

Fränkel, M. & Runge. (1) Old R. or R. waste treated with solvent, with or without pressure, and a strongly alkaline solution. Solvent is then removed by distillation.

Heinsohn, G. (1) Artificial latex prepared in the laboratory.

Koller, P. (1) See *Ammonia*.

Lascelles-Scott, W. (3) Borax water solution of R. A 2-2.5% aqueous solution of saponified R. resin will emulsify and hold a large amount of R. in a "milky state." R. is emulsified and dissolved by an aqueous solution of borax.

Plauson, H. (2) Solutions of R. in dil. caustic made in the Plauson mill.

Siever, R. W. (1) Emulsified R. in aqueous NH<sub>3</sub>.

Tuttle, J. B. (4) Water dispersions of R.

#### Latex—Uses for.

Anon. (52) Direct use of latex. The Hopkinson process. (143) Direct application of latex to fabrics. S may be added to latex. (239) Hancock, Thos. (1825) saturated rope or yarn with latex which was then coagulated and a waterproof coat was obtained. Bamber adds a solution of S to latex prior to coagulation with acid. Resulting mixture used in making R. articles. Physical quality of the R. is improved and R. does not become tacky. (239) Latex may be colored with dyes, such as methylene blue, and then coagulated. This idea was proposed by Hancock in 1857.

Bamber, M. K. (2) Vulcanizing agents and pigments incorporated into latex prior to coagulation with acid.

Biddle, A. (1) Casein, S and fillers mixed into latex and used to manufacture R. articles.

Brereton, C. A. (1) Latex for mfg. of paving, sheeting, roofing, etc.

Brittain, P. (1) Latex for coating materials with R.

Clark, P. H. (1) Direct use of latex in manufacture of R. goods, roadways, etc.

Hancock, T. (8) Direct use of latex for waterproofing, textiles, leather etc. Compounding ingredients were added.

Harris, G. (1) Latex of "Ficus Indica" applied to fibres, lines, twine, canvas and sail cloth.

Hopkinson, E. (1) Treatment of threads with latex.

Kaye, F. (5) Latex in paper making. (6) Latex paper.

Laub, G. C. H. (1) Addition to latex during coagulation of S and/or any other vulc. agent and any other substances required, to impart to R. when vulc., specific required qualities. (2) Admixture of S and/or any other vulc. agent with fresh latex during coagulation to give a coagulum which may be vulc. after drying without addition of vulcanizing ingredients.

Luff, B. D. W. (2) Review.

Morisse, L. P. T. (2) Latex poured into molds and coagulated by solution of Beechwood creosote, guaiacol and alcohol. 25 gm. H<sub>2</sub>SO<sub>4</sub> per liter of latex is then added. Latex is

coagulated, sterilized and vulcanized. Vulc. is effected by  $\text{H}_2\text{SO}_4$ . Balata and gutta percha latices need not be vulc.

Peel, S. (1) Waterproofing leather, cotton, etc.

Pinching, H. G. (1) Shipment of latex. Schidrowitz, P. (51) Manufacture of adhesives.

Schidrowitz, P. & Goldsbrough, H. A. (4) Latex coagulated to produce a spongy coagulum which is then fixed by vulc.

Société française de la Viscose. (1) The mixture of R. and cellulose may be obtained by mixing viscose and latex. Coagulation may be effected by  $(\text{NH}_4)_2\text{SO}_4$ . The R. in the mixture may be vulcanized with S vapors or  $\text{S}_2\text{Cl}_2$ . Schweizer's cupro-ammoniacal solution may replace viscose.

Stevens, H. P. (72) Comments on the direct use of latex.

#### **Latex-Vulcanization of.**

Anon. (14) Review of Bamber (1) on vulc. of latex.

Bamber, M. K. (1) See Sulfur Chloride.

Dunston, W. R. (1) Bamber added  $\text{S}_2\text{Cl}_2$  to latex and prepared vulc. R. Reid, Charles. (1) Latex sprayed into a cone of air,  $\text{SO}_2$ , or  $\text{H}_2\text{S}$ ,  $\text{S}_2\text{Cl}_2$  or other gas suitable for producing vulc.

Schidrowitz, P. (52) Aqueous solution or colloidal suspension of vulc. R. prepared by vulc. of uncoagulated R. latex. Piperidine or aldehyde ammonia or sodium polysulfides, sulfur and  $\text{ZnO}$  added to ammonia preserved latex and cured 30 min. rise to  $286^\circ\text{F}$ . and 20 min. at  $286^\circ\text{F}$ .

#### **Lauth's Violet.**

Bedford, C. W. & Sebrell, L. B. (1) An accel.

#### **Lead (metallic). See Metals.**

Thomson, W. & Lewis, F. (1) See Copper.

#### **Lead Abietate.**

Lascelles-Scott, W. (15) Retards decomp. of  $\text{PbS}$  and helps to keep its color. (28) Pb abietate enables white lead to be used without injuring the R. Mixture of Pb abietate and white lead is more slowly discolored by S compounds. See Resins.

#### **Lead Acetate.**

Breuil, P. (3) Goodyear & Payen used it to make semi-hard rubber.

Goodyear, C. (5) Has no drying action on tacky R.

#### **Lead Alkyl Derivatives.**

Marzahn, R. (1) p. 467. Accels. of vulc.

Spence, D. (29).

#### **Lead Bromide. See Antimony Iodide.**

#### **Lead Carbonate. See White Lead.**

Goodyear, Chas. (1) Vulc. of R. at high temp. using S and carbonate, oxide or other lead compounds. See Meyer, L. O. P. (9).

Marcy, E. E. (1) See Zinc Hyposulfite and Lead Protoxide.

#### **Lead Chromate.**

Anon. (178) Oxidizes R. making it brittle and hard.

Breuil, P. (3) C. O. Weber states that it may be used in cold cured but not in hot cured goods.

#### **Lead Dithiocarbamates. See Dithiocarbamates.**

Molony, S. B. & Nikaido, Y. (1) Lead dithiocarbamates do not function at as low a temp. as the zinc salts.

Ostromuiskii, I. (31) See Isoamylamine-isoamyl-dithiocarbamate.

#### **Lead Hyposulfite. See Lead Thiosulfate.**

Thomas, J. (1) A mixture of lead sulfide and lead hyposulfite used as a vulcanizing agent.

Moulton, S. (1) (3) Used mixture of lead or zinc hyposulfite or with lead sulfide or zinc sulfide with or without magnesium carbonate to vulcanize R.

#### **Lead Iodide. See Antimony Iodide.**

Fawsitt, C. A. (3) Lead iodide and S used for vulcanizing R.

#### **Lead Mercaptides.**

Bedford, C. W. & Sebrell, L. B. (2) Accels.

#### **Lead Oleate.**

Dannerth, F. (1) 5 pts. lead oleate is equivalent to 3 pts.  $\text{PbO}$ . Does not "burn" the R. mix. Prevents blooming of S. Non-poisonous.

- Kratz, G. D. & Flower, A. H. (2) Foot-note. More active an accel. than PbO.
- Pickles, S. S. (4).
- Schulze, E. (11) Mentions the use of lead soaps.
- Spence, D. (28) Sodium and lead oleate act as accels. of vulc.
- Weber, L. E. (9) Questions non-poisonous properties of lead oleate.
- Lead Oxide.** See Litharge and Red Lead.
- Lead Oxychloride.**
- Breuil, P. (3) Accelerates vulc. It is not used in R. industry.
- Lead Peroxide.** See Red Lead.
- Lead Phenate (phenolate).**
- Pickles, S. S. (4) An accel. of vulc.
- Lead Protoxide.**
- Marcy, E. E. (1) R. is vulcanized with lead sulfide and carbonate or protoxide without the use of free S. See Zinc Hyposulfite.
- Lead Resinate.**
- Price, R. B. (1) See Thiocarbanilide.
- Lead Salts of Dithio-acids.**
- Cadwell, S. M. (5) (6) Mentioned as accels.
- Lead Stearate.**
- Dannerth, F. (1) Accelerates vulc.
- Lead Sulfate.**
- Dubosc, A. (45) Lead sulfate is separated from lead sulfide and lead carbonate by extracting the R. with chlorhydrin saturated with HCl.
- Lead Sulfide.**
- Anon. (148) PbS mentioned as a R. pigment in 1887.
- Bernstein, G. (6) Use of oxidizing agents in a R. mix to oxidize PbS to PbSO<sub>4</sub> and prevent dark coloration. Sodium perborate, chlorates, chromates, persulfates and barium dioxide.
- Bolas, T. (3) A vulcanizing agent of R.
- Breuil, P. (3) Marzahn, R. & Weber, C. O. state that PbS accelerates vulc. Esch, W. says it does not. "Eureka" or "Burnt Hypo" found by Marzahn to be a mixture of PbS and S and offers special advantages in R.
- Ditmar, R. (47) p. 103. PbS as a vulcanizing agent.
- Esch, W. (2) PbS is inactive in vulc. processes.
- Gerner, H. (2) See Mercuric Sulfide.
- Lascelles-Scott, W. (26) Assists vulc. even when small amounts are used.
- Marcy, E. E. (1) See Zinc Hyposulfite and Lead Protoxide.
- Marzahn, R. (1) p. 467. An accel. of vulc.
- Moulton, S. (1) (3) Used a mixture of lead or zinc hyposulfite with lead sulfide or zinc sulfide for vulc. of R. MgCO<sub>3</sub> may be used.
- Pearson, H. C. (1) p. 63. Artificial sulphuret of lead. p. 68. PbS assists the resiliency of para compounds.
- Pickles, S. S. (4) Mentions lead polysulfides.
- Sandmann, D. (1) R. from latex coagulated with NaF is vulc. with S and PbO without the formation of PbS.
- Schulze, E. (1) See Litharge.
- Seidl, E. (1) PbS is not an accel.
- Turner, W. A. (2) R-3, BiS and PbS mixture-1. Cure 138°-142° C. The cured R. withstands a temp. of 200° C. without becoming hard and brittle.
- Lead Thiocarbanilide.**
- Bedford, C. W. & Sebrell, L. B. (2) Thiocarbanilide forms a lead mercaptide.
- Lead Thiosulfate.** See Lead Hyposulfite.
- Breuil, P. (3) A vulcanizing agent of R.
- Gottlob, K. O. (6) p. 70. Prevents sulfur bloom.
- Lascelles-Scott, W. (26) Gives good ageing R. compounds.
- Marzahn, R. (1) p. 467. Assists the vulc. of R.
- Weber, C. O. (1) Has some vulcanizing action. (61) p. 183. A vulcanizer rather than an accelerator. Composition and analysis.
- Lead Xanthates.** See Xanthates.
- Leucine.**
- Gorter, K. (11) Leucine has scarcely any accelerating action on vulc.

**Leuco bases.**

- Meus, E. de. (1) Mentioned as accelerators.
- Light.** See Acetone Peroxide, Ageing, Ageing-Oxidation, Ageing-Tackiness, Depolymerization, Heat.
- Anon. (114) Crude R. more sensitive to light than vulc. R. (236) Action of light and other agents on R.
- Ahrens, F. (1) See Viscosity.
- Bernstein, G. (1) Vulc. by light of R. containing S, sulfides or S containing substances, at 65-80° C. Ultra-violet rays deteriorate unvulc. R. (2) Effect of light on viscosity, depolymerization and vulc. (3) See Depolymerization.
- Bertrand, G. (1) Light decomposes R. See Ageing-Tackiness.
- Brindejone, G. (1) Action of light, temp., sea water, acetic acid and phenol on Landolphia Hendelotii. Tackiness is increased. See Ageing-Tackiness.
- Burke, W. H. (1) Vulc. R. by golden Sb sulfide and exposure to light.
- Clouth, F. (1) p. 131. (English Edition) p. 150. Vulc. thin sheets of R. and S by action of light.
- Dastre. (1) Ultra violet light will vulc. a R-S solution at ordinary temp. in 6 seconds.
- Ditmar, R. (2) Gamma rays from radium barium bromide preparation pass thru raw R. more readily than thru vulc. R. Radio activity persists longer in R. than in other similar solids. (62).
- Dubosc, A. & Luttringer, A. (1) p. 135.
- Dyer, J. W. W. (1) Ultra violet light attacks cotton faster than R. PbO in R. protects against light by forming colloidal PbS. Toluene-azo-toluene-azo-beta-naphthol protects R. against oxidation in light. Tension in airship fabrics increases action of light on the R. Heat and artificial light tests are of no value on balloon fabrics.
- Eder & Toch. (1) Observations in 1881 on effect of light on viscosity of R. solutions.
- Esch, W. (7) Clouth (1) had no combined S in his vulc. by the action of light.
- Hayward, N. (1) See W. C. Geer (5) p. 22 & Pearson, H. C. (1) p. 54 S spread on the surface of R. and vulc. in sunlight.
- Heil, A. & Esch, W. (1) p. 62. No trace of combined S on exposing thin sheets of R. and S to sunlight. See Clouth (1) above.
- Heilbronner, A. & Bernstein, G. (1) Vulc. of a R. gel by S and ultra violet light. 0.6% Sc gives a stable gel. (2) Ultra violet light completely depolymerizes R. in 7 sec. S repolymerizes same in 56 sec. (3) Vulc. of R. in solution by light.
- Henry, V. (5) First use of ultra violet light for vulc. of R. Light affects crude R. faster than vulc. R. Mineral fillers such as PbO resist action of light. Sb sulfides promote the same. Light is inactive in absence of oxygen.
- Hinrichsen, F. W. (8) See Tetra-bromide of Rubber.
- Kogakushi, K. (1) See Ageing-Tackiness.
- Lewis, S. J. & Porritt, B. D. (1) Determination of the wave lengths of light absorbed by R.
- Mannich, C. (1) Claim of priority over Schopper (1).
- Olivier, H. P. M. A. (1) Ultra violet light will vulc. R. with S or with CS<sub>2</sub>, allyl sulfide, Sb sulfides, etc., which are decomposed by the rays giving active S.
- Ostromuilenskii, I. (1) Polymerization of unsaturated hydrocarbons by ultra-violet light. (12) Vulc. by O<sub>2</sub> and ultra-violet light at 40-80° C. followed by a cure in vacuo at 120° C. Soft R. or ebonite are obtained. (17) Ultra violet light changes O<sub>2</sub> to O<sub>3</sub> and S<sub>2</sub> to S<sub>8</sub>. Both ozonides vulc. R.
- Paterson, C. C., Rayner, E. H. & Kinnes, A. (1) See Ebonite.
- Plotnikow, J. (1) Ultra-violet light polymerizes vinylchloride to "Rubber Chloride" (CH<sub>2</sub>=CHCl)<sub>n</sub>.
- Porritt, B. D. (6) Air produces no viscosity change in R. in absence of light. Light induces vulc. by S. Protection of R. from light by use of dyes and colloidal PbS.
- Raybaud, L. (1) Balloon envelopes deteriorate in the ultra violet rays at

- high altitudes. Red and yellow pigments used for protection. Red pigments preferred.
- Repony, D. (3) Oxidation by light is more rapid than by heat alone. Action of light on unvulc. R.
- Rieder, J. (1) R. as a light sensitive material for photographic purposes. A R. film is exposed to light under a positive, then dusted to bring out contrasts.
- Schopper, T. (1) Beta-methyl dihydroxy cumarine or dimethyl-amino-beta-methyl cumarine used in balloon fabrics to prevent deterioration by light.
- Seeligmann, Torrilhon & Faleonnet. (1) p. 131 & 203. Vulc. retards action of light and air on R.
- Seely, M. (1) S combines with R. in the presence of light but not in its absence.
- Simpson, W. (1) R. becomes brittle in light giving a product soluble in alcohol.
- Spence, D. & Kratz, G. D. (1) Light accelerates changes in viscosity.
- Stern, E. (4) Ultra violet, Röntgen and Radio active rays for vulc. of R.
- Stevens, H. P. (45) Light may cause a R. cement to gel and later to become fluid again. This may be repeated.
- Swan, J. W. (1) An early observation on the effect of light on oxidation.
- Terry, H. L. (16) Discussion of Porritt (6).
- Thomas, V. (1) Vulc. with S by the aid of violet or ultra violet light.
- Thomson, W. (1) Light has no effect on R. in absence of O<sub>2</sub>.
- Tuttle, J. B. (3) Action of heat and light on vulc. R.
- Vernet, G. (2) Action of light on vulc. R.
- deVries, O. (24) p. 351. Action of light on R.
- Lime.**
- Anon. (122) Similar to PbO in its action. (129) Basic carbonates of lime used in R. compounds. (255) An accel. of vulc.
- Beadle, C. & Stevens, H. P. (4) Lime forms sulfides and sulfates during vulc. and turns dark reddish yellow in color. (16) Accelerates vulc. but compound ages poorly.
- Breuil, P. (8) Facilitates vulc. but increases hardness and decreases the strength. Used to dry up R. Inferior to MgO. Antimony sulfide gives violet color with lime and loses its effectiveness.
- Ditmar, R. & Thieben, R. (1) Lime reacts with S in 45 min./4 atm. to produce sulfides and sulfates. See Compounding Ingredients.
- Dubosc, A. (63) Lime and MgO give poor ageing compounds.
- Endres, H. A. (1) Comparison of organic and inorganic accel.
- Esch, W. (13) See Protein.
- Foden, N. (1) Lime causes R. to age poorly.
- Gerard, A. (1) Gerard's alkali process R-100, S-6, Lime-6 to 10. Cure 1½ to 3 hrs. in steam or hot water.
- Goodyear, N. (1) See Ebonite.
- Gottlob, K. O. (6) p. 70 & 115. Either calcined or slaked lime acts as an accel.
- Goodyear, C. (5) Lime used to whiten unvulc. R.
- King, A. H. (1) ½ to 2½% used in soft rubber. Hard rubber requires more.
- Kratz, G. D. & Flower, A. H. (2) Comparison of Lime and Magnesia. Tables of tests and combined S.
- Martin, W. G. (1) Lime is undesirable in R. from the ageing standpoint.
- Marzahn, R. (1) p. 271. Reference to vulc. of R. by heating with 3% to 10% lime by Gerard.
- Maximoff, A. (1) Almost inert with thiuram mono- and disulfides.
- Ostromuiskenskii, I. (19) & (21) Lime activates nitro compounds in cures without S.
- Peachey, S. J. (11) Except when used in small amounts, lime causes hardening during ageing.
- Pearson, H. C. (1) p. 87 & 102.
- Pickles, S. S. (4) Lime acts differently in steam cures than in mold cures. (6).
- Porritt, B. D. (1) p. 41. Accelerates vulc.
- Potts, H. E. (4).
- Price, R. B. (1) See Thiocarbanilide.
- Schidrowitz, P. (6) p. 190. Used to accelerate and improve vulc. of R.

- (14) Lime gives tensile and snap at the expense of distensibility and resilience. Organic accels. give both.
- Schulze, E. (7) Effect of S and lime on the vulc. of R. (1898). Lime accelerates vulc. and by this function prevents porosity, rather than by absorption of moisture.
- Scott, W. & Bedford, C. W. (1) Lime does not function well in deresinated rubbers.  $H_2S$  is necessary for its action.
- Seidl, E. (1)
- Simmons, H. E. (1).
- Smith, A. H. (1).
- Springer, G. (1) Lime neutralizes free acids and is an aid in the vulc. of R.
- Stevens, H. P. (21) Has about 1/7 the curing power of  $MgO$ . Tends to form polysulfides. (41) Saccharated solution of lime as a coagulant for latex.
- Tassilly, E. (1) p. 211.
- Terry, H. L. (1)  $CaSO_4$  forms during vulc. (15) p. 141. (17) An accel. of vulc. Preparation and impurities of hydrated lime.
- Twiss, D. F. & Brazier, S. A. (1).
- Ure, A. (2) Quicklime added to R. to dry the same. Description of machines and processes used in R. industry.
- Weber, C. O. (45) Calcium hydrate and not the oxide used for R. compounding in 1903. "Supposed to act as a drier." (49) See Sulfur.
- Litharge.**
- Alexander, P. (7) Rapid vulc. of reclaimed R. is due to presence of  $PbO$ .
- Anon. (50) Precautions in England in factory use of  $PbO$ . (111) Lead poisoning. (122)  $PbO$  is probably most energetic inorganic accel. Antimony sulfide,  $MgO$  and lime give analogous results. The oxides probably give  $SO_2$  in presence of S, which reacts with  $H_2S$  from the resins and S to form colloidal S which unites with the R. (172) Lead oxides with S exert an oxidizing influence on R. and make it oil resistant. (230). (240) Certain resins in combination with  $PbO$  accelerate vulc. better than  $PbO$  alone. (255)  $PbO$  diminishes the action of organic accels. (294) Litharge poisoning.
- Bayer & Co. (34) Use of  $PbO$  with amine accels.
- Beadle, C. & Stevens, H. P. (4) Sulfides and sulfates are formed during vulc.
- Bean, P. L. (1) See Piperidine-pentamethylene-dithiocarbamate.
- Bedford, C. W. & Sebrell, L. B. (2)  $PbO$  forms lead mercaptides with mercapto accels. including thiocarbamilide.
- Bernstein, G. (6) See Lead sulfide.
- Bourn, A. O. (1) R.-100, S-3,  $PbO$ -50, Whiting-50, vulcanizes to good cure in 1 second at  $600^\circ F.$  or in 211 days at  $105^\circ F.$
- Breuil, P. (3).
- Brooks, B. T. (1) p. 136.
- Ditmar, R. (21) Vulc. with  $PbO$  in steam and dry heat. (35) See Zinc Oxide. (47) p. 102. (49) p. 13. The action of  $PbO$  is exothermic.  $PbO$ ,  $MgO$ ,  $CaO$ ,  $MgCO_3$  and  $CaCO_3$  all form sulfides and sulfates during vulc. (62)  $PbO$  and  $MgO$  combined give greater effect than the summation effect of each alone.
- Ditmar, R. & Thieben, R. (1) 10 gm.  $PbO$  and 2 gm. S, heated 45 min./4 atm. 66.06% of the S is chemically combined as sulfide and sulfate. See Compounding Ingredients.
- Dubosc, A. (30)  $PbO$  reacts with S to form sulfur dioxide. See Sulfur Dioxide. (44) Determination of  $PbS$  in litharge stocks. (45) Determination of  $PbSO_4$  in litharge stocks.
- Eaton, B. J. & Grantham, J. (3) The use of  $PbO$  obscures the variability of plantation R.  $MgO$  added to a compound containing  $ZnO$  does not reduce the difference in the rate of cure between fast and slow curing rubbers.
- Esch, W. (2) & (9) Action of  $PbO$ .  $PbS$  is inactive. (6) p. 71. Curing power of  $PbO$  is due to heat of reaction with S.
- Esch, W. & Auerbach, M. (1) Action of  $PbO$  attributed to the heat of formation of  $PbSO_4$ .
- Goodyear, Chas. (1) First use of litharge in R. See Lead Carbonate. (4) p. 155. White lead or  $PbO$  causes

- R. articles to be more readily changed or vulcanized.
- Goodyear, N. (1) See Ebonite.
- Gottlob, K. O. (6) p. 70 & 115. Discussion of inorganic accels.
- Grove, J. M. (1)
- Hamilton, A. & Luce. (2) Litharge poisoning.
- Heil, A. & Esch, W. (1) p. 60. Used to increase the amount of S combined with the R.
- Heilbronner, A. (1) Reducing agents such as pyrogallol and tannins prevent the blackening of PbO stocks. See Tannin.
- Hoffer, R. (1) p. 79.
- King, A. H. (1) 1% S required for each 7% PbO. High PbO prevents blooming.
- Kirchhof, F. (7) R. vulc. with PbO or PbS with a small amount of a S and a small amount of a S free organic catalyst.
- Klein, C. A. (1) Rubber factory hygiene.
- Marzahn, R. (1) p. 85.
- Meeus, E. de (1).
- Murdock, H. R. (1) Zinc sulfate compounded into PbO stocks to change the PbS to PbSO<sub>4</sub> and thus prevent the blackening of the cured stock.
- Ostromuiskenskii, I. (13) PbO as an activator for dithiocarbamates. (14) PbO more active than MgO and ZnO in absence of amines, while with them it is less active. Its action is attributed to the liberation of oxygen.  $PbO + S = PbS + O$ . (19) PbO is the strongest activator for nitro compounds. (21) PbO activates nitro compounds for vulc. without S.
- Peachey, S. J. (4) PbO retards the action of accels. (11) Disagrees with E. Seidl on the thermal action of PbO. With 5% PbO there is no rise in temp. PbO retards the action of Accelerene.
- Pearson, H. C. (1) p. 103.
- Pickles, S. S. (3) Effect of resins on PbO during vulc. (4) The action of PbO is dependent on some constituent of the R. (6).
- Porritt, B. D. (1) p. 41.
- Potts, H. E. (4) PbO raises the temp. of the article during cure thus causing a higher reaction velocity by burning up the protein and resins in the R. which exert the function of fuels. PbO is not deleterious to R.
- Rossem, A. van. (6) Comparison of PbO with other accels. by coefficient of vulc.
- Sandmann, D. (1) See Hydrofluoric Acid.
- Schidrowitz, P. (6) p. 190. (49) See Poisoning.
- Schulze, E. (11) Action of PbO as an accel. is due to heat conductivity and formation of lead soaps. PbS has no effect on vulc. but both PbS and PbO hasten vulc. by acting as heat conductors. Hardening effect of PbO probably due to saponification of R. resins.
- Scott, W. & Bedford, C. W. (1) PbO is a secondary accel. since it activates the nitrogen in the resins and proteins by causing them to react with S.
- Seidl, E. (1) Curing power of PbO is not due to thermal conductivity. PbO and S give off little heat at vulc. temp. except in the presence of organic bodies, such as aniline, phenol, R. resins, etc. PbO accelerates the reaction between S and resins and its curing power is attributed to the heat produced by this reaction. See Hydrogen Sulfide.
- Sevier, W. (1) PbO, Pb acetate or Zn sulfate added to R. cements as "drying agents" (1835).
- Simmons, H. E. (3).
- Smith, A. H. (1).
- Spence, D. (28).
- Stevens, H. P. (2) PbO capable of replacing insoluble matter of R. as an accel. of vulc. (3) 17.5 pts. PbO is best proportion for maximum vulc. Excess PbO lowers the Sc. Some S always remains uncombined. PbO accelerates due to heat formation of PbS and PbSO<sub>4</sub>. (4) Estimation of PbS and PbSO<sub>4</sub> in vulc. R. (5) Litharge stocks will not cure if the R. has been previously acetone extracted. Corroborates L. E. Weber. Removal of resins causes compound to perish rapidly. (7) PbO eliminates variability in plantation R. (10) Comparative tests with R-S-PbO mixings. The presence of non-rubber, acetone-soluble materials are necessary for the vulc. of R. in the



presence of PbO. (16) MgO is more powerful than PbO weight for weight. Comparison of PbO, MgO, Accelerene and a basic accel. by tensile and coefficient of vulc. (48) Effect of PbO on variability tests. (64) PbO and ZnO in slab rubbers prepared with various coagulants. Coeff. of vulc. is higher for the more slowly vulcanizing rubbers. (70) Crude R. tests using PbO. (75) See Sodium Silicofluoride and Enzymes.

Tassilly, E. (1) p. 212.

Terry, H. L. (3) PbO takes up the excess S which if left in the R. in the free state would prove detrimental to the R. articles.

Thomas, V. (1) PbO is a catalyst for vulc. by the aid of ultraviolet light.

Tuttle, J. B. (1) See Natural Accelerators.

Twiss, D. F. & Brazier, S. A. (1).

Weber, C. O. (1) PbO combines with the excess S to form PbS and prevent "bloom." ZnO is inactive in this respect. (44) Reactions during vulc. PbO exerts a polymerizing action on R. which has become depolymerized in mixing and heating. (45) PbO toughens R. but does not increase elasticity. PbO acts as a S carrier. (48) PbO is a vehicle for S in the addition of S to R. during vulc. by the formation of PbS. (56) The presence of oxygen compounds in R. slows up the cure. These rubbers are improved by adding PbO. (61) p. 185.

Weber, L. E. (2) Resin free rubbers will not cure with PbO. In the discussion of this paper G. H. Savage reports experiments showing a chemical action between R. resins and PbO. Part of the resin is destroyed or rendered insol. in acetone during vulc.

Williams, H. J. (1) Pt. III. Manufacture and use of lead oxides in R. (2) Lead compounding ingredients in 1892.

Zsigmondy, R. & Spear, E. B. (1) p. 256. PbO is an accel. for black goods. MgO and lime for white goods.

**Lithium Salts of Thiol acids.** See Xanthates.

**Lithium Xanthates.** See Xanthates.

**Lithopone.** See Compounding Ingredients.

**Lupeol.**

Cohen, N. H. (1) Crude balata yields a lupeol acetate in addition to beta-amyrin acetate and beta-balalban. Lupeol acetate (m.p. 208°-210° C.) on hydrolysis gave lupeol (m.p. 210° C.). (2) Lupeol is not found in African R. See Amyrin Acetate. (3) Bresk or dead Borneo (similar to gutta percha) contains lupeol ( $C_{31}H_{50}O$ ) and alpha- and beta-amyrin. (5) Para R. does not contain lupeol.

Romburgh, P. van. (2) Lupeol from gutta percha is not acetylated by sodium acetate and acetic acid but is converted to hydrocarbon by dehydration.

**Lupeol Acetate.**

Cohen, N. H. (1) Found in crude balata. Lupeol acetate (m.p. 210° C.) in balata is not identical with synthetic lupeol acetate, m.p. 215° C. See Lupeol.

Hillen, G. H. (1) Found in Jelutong or Pontianac R. See Resins.

Ultee, A. J. (16) In Ficus Vogelii. See Alpha-Amyrin Acetate.

**Lupeol Cinnamate.**

Hillen, G. H. (1) Found in the resin of a gutta percha from German New Guiana.

**Magenta.**

Gaisman, L. & Rosenbaum, J. L. (1) An accel.

**Magnesia.**

**Magnesium Oxide.**

Anon. (47) An accel. which can be easily milled into R. (122) Analogous to PbO in its action. (223) Magnesia is more suited than lime as an aid in vulc. (255) MgO increases the action of organic accels. Badische Co. (6) MgO used with piperidine.

Beadle, C. & Stevens, H. P. (4) MgO and  $MgCO_3$  both form sulfides and sulfates during vulc. Tabulated data of effect of MgO on Sc.

- Bedford, C. W. & Scott, W. (2) After acting as a secondary accel. MgO acts as a primary accel. It forms a polysulfide solution when suspended in water with S and H<sub>2</sub>S.
- Breuil, P. (2) MgO gives good results in African, resinous and slowly vulcanizable or other tacky rubbers. Guayule vulcanizes poorly without it. Acts more as filler than a coloring pigment or accel. of vulc.
- Brooks, B. T. (1) p. 136.
- Ditmar, R. (16) Maximum tensile strength obtained with 30% heavy magnesia and maximum elasticity with 25%. (17) Light calcined magnesia increases strength and elasticity of R. compounds. (62) MgO and PbO combined give higher acceleration than the summation of the effect of either alone. (35) See Zinc Oxide.
- Ditmar, R. & Thieben, R. (1) 10 gm. MgO and 2 gm. S heated 45 min./4 atm. 80.5% of the S is chemically combined. Sulfides and sulfates are formed.
- Dubosc, A. (17) Chas. Goodyear reported the use of PbO, MgO, Lime and MgCO<sub>3</sub> in R-S mixes. (30) Attributes the accelerating power of MgO to occluded air, since its reaction with S is endothermic. Must be used in small amounts as it oxidizes the R. and makes it brittle. (56) 1 kilo heavy calcined MgO contains 1.10 c.c. of air. 1 kilo of light calcined MgO contains 3 c.c. of air. (63) See Ageing-Oxidation.
- Endres, H. A. (1) Comparison of organic and inorganic accels.
- Ephriam, J. (1) See Naphthol.
- Esch, W. (4) See Protein. (5) Heavy calcined MgO shows higher Sc than light calcined. (6) p. 69. Chas. Goodyear used MgO in R. MgO reacts with S. during vulc.
- Fol, J. G. & Heurn, F. C. van. (1).
- Frank, F. & Marckwald, E. (2) Vulc. coefficients.
- Goodyear, Chas. (4) p. 102. The tacky surface of R. was dried up by compounding with MgO. p. 104. Lime was found to give better results than MgO.
- Goodyear, N. (1) See Ebonite. Used MgO in Ebonite in 1851.
- Gottlob, K. O. (6) p. 70 & 115.
- Greider, H. W. (2) Light MgO as a compounding ingredient. Data on use with Hexa.
- Heil, A. & Esch, W. (1) p. 60 & 63. Used to speed up the cure and increase the Sc.
- Hoffer, R. (1) p. 79.
- King, A. H. (1) MgO has about one-half the curing power of lime. Does not harden the R. like lime. Works well with PbO. The best grade is heavy calcined MgO made from precipitated carbonate.
- Kratz, G. D. & Flower, A. H. (2) Comparison of light and heavy calcined MgO with organic and inorganic accels. Tables of constants and coefficients. MgO is a secondary accel. and its action is limited by the amount of nitrogenous substances present in the R. A high MgO-ZnO stock has a lower coefficient at maximum cure than the same stock without accel. Heavy MgO is less active than an organic accel. consisting of the condensation product of an amine and HCHO.
- Lehman & Vos. (1) Light MgO carries more air into a R. mix than the heavy MgO.
- Luttringer, A. (2) The effectiveness of inorganic accels. is dependent on the fineness of the particle. Especially true of MgO.
- Marckwald, E. & Frank, F. (7) Comparison of various grades of MgO. Specific gravity of article is unaffected by the magnesia used. With para R. containing MgO it was generally impossible to extract the resin present in R. Articles containing light MgO are not more easily oxidized than those containing heavy MgO. Light MgO gives higher tensile strength and elongation than heavy MgO. (8) MgO without S has no curing action. It only hastens S addition. See Sulfur Chloride. (11) MgO forms an intermediate product which accelerates the combination of S with R.
- Marzahn, R. (1) p. 329. MgO is of value in African rubbers containing high resin content.
- Maximoff, A. (1) Almost inert with thiuram mono- and disulfides.

- Ogier, M. (1) Salts of Pb, dissolved lime, calcined Magnesia, etc., facilitate vulc. of R. (1875).
- Ostromuiskii, I. (13) See Piperidine - pentamethylene - dithiocarbamate. (21) (25) MgO activates nitro compounds in cure without S.
- Peachey, S. J. (4) MgO aids "Acceleration." (11) MgO hardens R. during ageing to a less extent than lime. Disagrees with E. Seidl on thermal action. Contrary to W. Esch, no MgSO<sub>4</sub> is formed during the cure.
- Peachey, H. C. (1) p. 87 & 104.
- Pickles, S. S. (1).
- Porritt, B. D. (1) p. 41.
- Potts, H. E. (4).
- Rossem, A. van. (6) Comparison of MgO and other inorganic accels. by coefficient of vulc.
- Schidrowitz, P. (6) p. 190. (14) Calcined magnesia gives snap and tensile at the expense of distensibility and resilience. Organic accels. give both. (21) Quotes Kratz, G. D. & Flower, A. H. (2). The effect of MgO is dependent on the presence of nitrogenous substances.
- Seidl, E. (1).
- Simmons, H. E. (3).
- Smith, A. H. (1) Not over 2 pts. MgO should be used with 100 pts. of R. except with low S content.
- Spence, D. (28).
- Springer, G. (1) MgO is a good substitute for lime. Counteracts stickiness of uncured R. better than French chalk.
- Stevens, H. P. (16) MgO in small amounts is more active than PbO in promoting the combination of S with R. (21) Different samples of MgO vary 35% in curing power. Checks Kratz & Flower that light calcined MgO is more active than heavy calcined.
- Terry, H. L. (1) MgSO<sub>4</sub> does not form from MgO during the cure. (15) p. 141.
- Turpin, M. (1) Vegetable ivory is made by incorporating calcined MgO with R. and compressing the mixture in heated molds under high pressure. This material does not contain S. The density and tenacity of product are equal those of ivory.
- Twiss, D. F. (9) Résumé of work on MgO for 1911.
- Twiss, D. F. & Brazier, S. A. (1).
- Twiss, D. F. & Howson, C. W. H. (1) Curves of physical properties for light calcined magnesia.
- Weber, C. O. (11) Amount of MgO used depends on the method of cure. Direct Vapor—1.5-3% MgO; Press—5% MgO; Hot Air—10% MgO. (45) Action of ZnO, MgO, etc.
- Weber, L. E. (7).
- Whitby, G. S. (8) p. 392. Effect of PbO, MgO and Lime as accels. ZnO is almost without any accelerating value.
- Magnesium Bisulfite.**
- Magnesium Sulfite.**
- Heilbronner, A. (1) See Tannin.
- Magnesium Carbonate.**
- Breuil, P. (2) Acts as a pigment, coloring material and accel. of vulc.
- Ditmar, R. & Thieben, R. (1) 10 pts. of the carbonate heated with 2 pts. S for 45 min./4 atm. 7.2% of the S is combined. Sulfides and sulfates are formed.
- Gottlob, K. O. (6) p. 70. Acts only as a filler.
- Greider, H. W. (1) Light magnesium carbonate is both basic and hydrated.  $4 \text{ MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ . 9 volumes recommended as a filler. It has low curing power and gives a high permanent set.
- Porritt, B. D. (1) p. 42. An accel.
- Rossem, A. van. (6) Comparison with other inorganic accels. by coefficient of vulc.
- Scott, W. & Bedford, C. W. (1) Weak curing power of magnesium carbonate is due to its being a basic carbonate. Suspended in water with S and hydrogen sulfide a yellow polysulfide solution is formed. Its accelerating power is attributed to the formation of inorganic polysulfides.
- Springer, G. (1) Replacing whitening in "Steam goods" with magnesium carbonate tends to prolong the life of these articles.
- Magnesium Chloride.**
- Breuil, P. (2) Acts like calcium chloride in R. See Calcium Chloride.

Frank, F. (8).

Zimmerman, A. (3) Used as a coagulant for latex.

### **Magnesium Malate.**

Spence, D. (10) *Ficus Vogelii* latex has a high magnesium content, a crystalline product, probably magnesium malate, obtained from the serum.

### **Magnesium Oleate.**

Dannerth, F. (1) Accelerates vulc. and has lubricating properties.

### **Magnesium Polysulfide.**

Esch, W. (7) A powerful S carrier.

### **Magnesium salt of tetrahydroxy adipic acid.**

Gorter, K. (5) Found in latex of *Ficus Mastica*. The acid is identical with d-saccharic acid which has not been previously found in nature.

### **Magnesium salts of Xanthic, Thiol and other acids.**

Cadwell, S. M. (4) (5) (6) See Xanthates.

### **Magnesium Silicate.**

Ditmar, R. (32) Hancock used it to improve R. Patented Nov. 21, 1843.

### **Magnesium Stearate.**

Dannerth, F. (1) An accel. of vulc.

### **Magnesium Sulfate.**

Zimmerman, A. (3) Used as a latex coagulant.

### **Manganese. See Metals.**

Anon. (36) See Ageing-Oxidation.

Weber, C. O. (1) Manganese compounds even in small amounts are injurious to proofed goods. (9) Manganese does not affect dry heat proofed goods but is fatal to cold cured goods.

### **Manganese Borate.**

Lascelles-Scott, W. (13) This salt is harmful to R.

### **Manganese Dithiocarbamates.**

Molony, S. B. & Nikaido, Y. (1) & (2) See Dithiocarbamates.

### **Manganese Oxide.**

Bruni, G. & Pelizzola, C. (1) Causes tackiness in R.

Ditmar, R. (62) An energetic accel. of vulc. Softens R. on the mills. The vulc. R. ages badly.

King, A. H. (1) A strong accel.

Lascelles-Scott, W. (13) Harmful to R. Ostromuiskenskii, I. (11) (19) See Vulcanization.

Weber, C. O. (1) Manganese compounds cause deterioration of R.

### **Manganese Sulfide.**

Anon. (156) Prevents porosity and blistering and increases toughness and life of the R. (159) & (172) MnS and other metallic sulfides reduce porosity and give better resistance to ageing.

Eaton, A. K. (1) Manganese sulfide (persulfide) as a vulcanizing agent for R. Formed by heating  $MnO_2$  with S.

Lascelles-Scott, W. (13) Harmful to R.

### **Manganese Xanthates.**

Cadwell, S. M. (2) (4) (5) (6) See Xanthates.

### **Matezit. $C_{10}H_{16}O_8$ . m.p. 181° C.**

Girard, A. (1) From Madagascar R.

### **Maturation of Rubber.**

See Natural Accelerators and Slab Rubber.

Eaton, B. J. & Grantham, J. (1) Maturing of R. increases the rate of cure until the 6th or 7th day. (5) Latex evaporated in vacuo gave a R. that cured as quickly as matured R.

Eaton, B. J., Grantham, J. & Day, F. W. F. (1) Maturation of wet coagulum and its bearing on the vulcanizing properties of the R. Acceleration of cure produced by maturation is due to bacterial action. Maturation is retarded by soaking in HCHO, 1% phenol, 0.1% mercuric chloride.  $NaHSO_3$  added to latex also retards maturation.

Stevens, H. P. (13) A base extracted from matured R. had a little less curing power than p-nitrosodimethylaniline. (25) The rate of cure first decreases and then increases with increasing thickness of the sheets. Pro-

duction of alkaline accelerating materials by aerobic bacterial changes. Exposure to air during ripening has no influence on speed of vulc. (42) Maturation of R. is chiefly anaerobic. Maturing in thin sheets produces more rapid vulc.

de Vries O. (17) Matured or slab R. cures faster than ordinary rubbers. (24) p. 240. Discussion of maturation of R.

Whitby, G. S. (8) p. 186. Discussion of maturation of R. See Pyrolidine.

#### **Melam.**

Dubosc, R. (40) An accel.

#### **Melamin.**

Dubosc, A. (40) Mentioned as an accel.

#### **Meldola's Blue.**

Guisman, L. & Rosenbaum, J. L. (1) An accel.

#### **Melem.**

#### **Melon.**

Dubosc, A. (40) An accel.

#### **Melting Point of Rubber.**

Ditmar, R. (41) 19 different rubbers have higher melting points than that which is necessary for good vulc.

#### **Menthol.**

Ostromuiskenskii, I. (13) & (22) A weak accel. when used with metallic oxides. See Colophony and Xanthogenates.

#### **Menthyl Ether.**

Ostromuiskenskii, I. (22) Used in vulc. of synth. R.

#### **Mercaptans.**

#### **Mercaptides.**

Bedford, C. W. & Sebrell, L. B. (1) (2) See Zinc Mercaptides. Mercaptans and dithiocarbamates dissolve ZnO in R. cements.

Jones, F. (2) Zn mercaptides dissolve ZnO in R. cements.

#### **Mercaptobenzothiazole.**

Bedford, C. W. & Sebrell, L. B. (1) (2) The mercaptan, its disulfide and metallic salts as accels. of vulc. The

disulfide and mercaptan are aided by ZnO.

Bruni, G. (6) An accel.

Bruni, G. & Romani, E. (1) Theory of vulc. Disulfides vulc. R. without the aid of free S.

Romani, E. (2) Methods of preparation of the mercaptan and of its Zn, Cd, Hg and Pb salts. Mentions the three monomethyl derivatives and dimercapto-p-p-dibenzothiazole.

Sebrell, L. B. & Boord, C. E. (1) Effect of substituents in benzene nucleus upon its activity as an accel. of vulc.

#### **2-Mercapto-5-methyl thiazole.**

Bruni, G. & Romani, E. (2) 1 to 3% with ZnO, PbO, CaO, MgO, or HgO cures R. and S in 5 min./120° C. The disulfide and metallic salts are also described.

#### **Mercury.**

Bolton, W. von. (1) Action of Hg vapor on R.

#### **Mercury alkyl compounds.**

Marzahn, R. (1) p. 467. Accels. of the vulc. of R.

Spence, D. (28) Alkyl derivatives of Pb and Hg as accels. of vulc.

#### **Mercury Dithiocarbamates.**

Molony, S. B. & Nikaido, Y. (1) & (2) See Dithiocarbamates.

#### **Mercury Halides (Bromide, Chloride, Iodide).**

See Phosphorous Thioiodide and Antimony Iodide.

Anon. (178) Mercuric iodide not suitable as a R. pigment.

Fawsitt, C. A. (4) Vulc. of R-S mixes by mercury iodides and bromides.

Lascelles-Scott, W. (31) Mercuric iodide is not permanent enough to be used as a R. pigment.

Parkin, J. (3) Mercuric chloride. One of the first latex coagulants that was proposed. Also acts as a disinfectant.

Pearson, H. C. (1) p. 95. Calomel hastens the vulc. of R.

Terry, H. L. (6) See Sulfur Chloride.

#### **Mercuric Oxide.**

Twiss, D. F. & Howson, C. W. H. (1) Curing curves with and without thiocarbamide.

**Mercury Salts.**

Glenny & Walpole. (1) Unvulc. R. does not absorb mercury salts from solution but the higher the sulfur content of the R. the greater is the amount of mercury absorbed.

**Mercuric Sulfide.**

Anon. (273) A R. pigment.  
Breuil, P. (9) Use of  $\text{HgS}$  in R.  
Camille, A. (18) R. containing  $\text{HgS}$  should not come in contact with metals such as Zn, Cu, Fe or Sn.  
Forster. (1) Acts as vulcanizing agent and coloring material of R.  
Gerner, H. (2) 75% of the S necessary to vulcanize R. may be replaced by the sulfides of Hg, Sb, Pb or Zn.  
Geuns, J. van. (1) Orpiment used in R. in 1848.  
Heinzerling, C. (1) p. 65. Has good vulcanizing properties. Used as coloring material.  
Lascelles-Scott, W. (31) Properties of  $\text{HgS}$  as a R. pigment.

**Mercury Xanthates.**

Cadwell, S. M. (1) (2) (4) (5) (6) See Xanthates.

**Metals.** See Copper.

Anon. (3) Molten lead has no effect on R. (36) Effect of manganese on R.  
Bolten, W. von. (1) See Mercury.  
Camille, A. (1) See Copper.  
Ditmar, R. (62) Mentions the action of colloidal metals.  
Esch, W. (10) Tin is used to obtain a polish on hard rubber. Aluminum, iron and steel are used for molds. Aluminum powder also used in soft R. goods. Amalgams which melt on the mill are also used. The amalgams may aid in preserving the R.  
French American Rubber Co. (1) Powdered Sb, Zn and Pb are mixed with R. and vulcanized in the regular manner.  
Hoffman, H. A. & Juve, W. H. (1) Finely divided metallic lead is mixed with petrolatum prior to mixing into R.  
Marzahn, R. (1) p. 338.  
Reithoffer, J. N. (1) Attaching soft R. to metals by an intervening layer of metallic sulfides and R.

Seeligmann, Torrilhon & Falconnet. (1) p. 205. Iron, copper and common alloys corrode vulc. R.

Terry, H. L. (15) Action of Cr on R. See Copper.

Thomson, W. & Lewis, F. (1) Cu is most harmful to R. Pt, Pd, Al and Pb act feebly on R. Mg, Zn, Cd, Co, Ni, Fe, Cr, Sn, As, Sb, Bi and Ag have no action on R.  $\text{CuO}$  is very destructive to R. and  $\text{AgNO}_3$  and  $\text{MnO}_2$  are almost as bad. Ferric, sodium, ammonium and Uranium nitrates have some action on R. but not as harmful as the above.

Turner, W. A. (1) Heat R. and S with Bi, Sn or Pb to give a better vulcanized product.

Warren, T. T. P. B. (2) Metals on vulc. R. dissolve S and cause devulcanization.

Weber, C. O. (13) Action of metals on R. (52) Metals influence the reaction of R. with S (vulcanization) and with oxygen (oxidation). The action of metals is greater the greater the affinity of the given metal for oxygen or S.

**Metallic Salts.**

Hancock, C. (1) Use of  $\text{NO}_2$  and  $\text{ZnCl}_2$  to improve the quality of gutta percha or R.  
Thomson, W. & Lewis, F. (1) Cold vulc. R. sheets were painted with solutions of metallic salts. R. entirely destroyed by  $\text{CuSO}_4$ ,  $\text{CuCl}_2$ ,  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Cu}_2\text{Fe}(\text{CN})_6$ ,  $\text{CuO}$ ,  $\text{CuS}$ ,  $\text{AsI}_3$ ,  $\text{AgNO}_3$ ,  $\text{Sr}(\text{ClO}_4)_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{MnO}_2$ ,  $\text{MnO}$ ,  $\text{BiCl}_3$ ; considerably affected by  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{NaNO}_3$ ,  $\text{V}_2\text{O}_5$ , Ammonium vanadate; slightly affected by  $\text{PbCrO}_4$ ,  $\text{FeSO}_4$ ,  $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ ,  $\text{ZnCl}_2$ ,  $\text{SnO}_2$ ,  $\text{SnCl}_4$ ,  $\text{PbB}_2\text{O}_7$ ; no action by  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{Cl}$ ,  $(\text{NH}_4)_2\text{CO}_3$ ,  $\text{K}_2\text{CrO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{KCN}$ ,  $\text{KC}_2\text{H}_3\text{O}_2$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{K}_2\text{ClO}_4$ ,  $\text{KI}$ ,  $\text{KNO}_3$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{NaCl}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{LiCl}$ , Lithium salicylate, Rubidium chloride,  $\text{MgO}$ ,  $\text{MgSO}_4$ ,  $\text{MgCl}_2$ ,  $\text{CaCO}_3$ ,  $\text{CaCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_2$ ,  $\text{Al}_2(\text{SO}_4)_3$ , Aluminum chlorate,  $\text{ZnCrO}_4$ ,  $\text{Zn}(\text{NO}_3)_2$ ,  $\text{ZnO}$ ,  $\text{ZnSO}_4$ ,  $\text{FeCl}_3$ ,  $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_3$ ,  $\text{MnCl}_2$ ,  $\text{CoCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{Ni}(\text{NO}_3)_2$ , Thallium chloride,  $\text{HgCl}_2$ ,  $\text{HgI}_2$ ,  $\text{H}_3\text{AsO}_4$ ,  $\text{H}_3\text{AsO}_3$ ,  $\text{Bi}(\text{NO}_3)_3$ ,  $\text{BiO}$ ,  $\text{CdBr}_2$ ,  $\text{CdCl}_2$ ,  $\text{CdI}_2$ ,  $\text{Cd}(\text{NO}_3)_2$ ,  $\text{CdSO}_4$ ,

PbCl<sub>2</sub>, Pb(C<sub>2</sub>O<sub>4</sub>), Tin proto chloride, Tin oxalate, Palladium chloride, Gold chloride. The smallest trace of CuSO<sub>4</sub> causes R. to lose its elasticity and become rotten in 9 days at 140° F. The presence of factis tends to prevent the harmful action of CuSO<sub>4</sub>.

**Methylamine.** See Aldehyde-Amines.

Bayer & Co. (28) Used to improve the ageing of balloon fabric. See Ageing.

Ditmar, R. (10) Odor of methylamine in latex exposed to air.

Dubosc, A. (54) Saturated solution of methylamine in cold furfural used as an accel. in hot air vulc.

Seeligmann, Torrilhon & Falconnet. (3) p. 93. Noted the odor of methylamine in fresh latex.

**Methylaniline.** See Aldehyde-Amines.

Badische Co. (8) Used in synth. R. to improve quality.

Gottlob, K. O. (8) A preservative for synth. R.

Kratz, G. D., Flower, A. H. & Shapiro, B. J. (1) See Aniline.

Ostromuiskii, I. (13). (17) Inactive as an accel. of vulc.

**Methyl Chloride.**

Camille, A. (13) Action on R.

Edwards, J. D. & Pickering, S. F. (1) Permeability of R. to methyl chloride, etc.

Lascelles-Scott, W. (4).

Pfaff, C. H. (1) R. swells in methyl chloride and becomes white in color.

**Methylcyclohexanone.**

Harries, C. (25) See Rubber Hydrochloride.

**Methyl esters of Dithiocarbamic acids.**

Molony, S. B. & Nikaido, Y. (2) Accels. of vulc.

**Methyl-ethylenyl-phenylene-diamine.**

Bastide, J. (1) Used as a solvent for sulfur in a mixing with R. to obtain better distribution of the S.

Stevens, H. P. (10) Advantage of this material is due to its accelerating rather than solvent action on the R.

**1-Methyl Inositol.** See Quebrachite.

Anon. (258) Found in Para and Hevea R.

Beadle, C. & Stevens, H. P. (17) See Latex.

Campbell, L. E. (2) Present in Hevea latex.

Jong, A. W. K. de. (2) Noted the presence of 1-methyl inositol in Hevea latex.

Maquenne. (1) Inosite and Dambonite are identical.

Pickles, S. S. & Whitfield, B. W. (1) Identical with quebrachite. Found in plantation R. up to 2½%, also in Asiatic and Para R. Its function in the latex.

Stevens, H. P. (13) Found in the serum from coagulated latex. (70) Inositol is not one of the active constituents of R. resins.

**Methyl Iodide.**

Camille, A. (13) An accel. for the vulc. of R. by S<sub>2</sub>Cl<sub>2</sub> giving uniformity.

**p - Methyl - phenylene - ammonium - p - methyl-phenylene-dithiocarbamate.**

Cadwell, S. M. (5) (6) An accel.

**Methyl Piperidine.**

Anon. (84) An accel. of vulc.

Bayer & Co. (5) & (6) An accel.

Ditmar, R. (62).

Eaton, B. J. (8).

King, A. H. (1).

Pearson, H. C. (1) p. 85.

**Methyl Succinic Aldehyde.**

Bayer & Co. (17) (18) See Ozone.

**Methyl Violet.**

Gaisman, L. & Rosenbaum, J. L. (1)

See J. L. Rosenbaum (1).

Meeus, E. de. (1) An accel.

Rosenbaum, J. L. (1) A strong accel. of low basicity. The color is not lost during vulc.

**Methyl Rubber.**

Hübener, G. (13) Bromination of.

**Methyl Xanthates.**

Cadwell, S. M. (1) (4) (5) (6) See Xanthates.

**Methylene Aniline.**

**Phenyl-imino-methane.**

**Anhydro formaldehyde aniline.**

**Formaldehyde Aniline.**

**Formanilide.****Trimethylene-trianiline.**

- Anon. (84).  
 Bastide, J. (1) See Methylene Diphenyldiamine.  
 Bayer & Co. (31) Uses 10% on the R.  
 Bedford, C. W. (1) & (4) This accel. is heated with S to form new accels.  
 Bedford, C. W. & Scott, W. (1) This accel. reacts with S at curing temp. to form thiocarbanilide and other thiourea derivatives. CS<sub>2</sub> and amines are also formed.  
 Bruni, G. (1) This accel. reacts with S to form mercaptobenzothiazole.  
 Dannerth, F. (1) Claims to have proposed the use of this accel. in 1917.  
 Dubosc, A. (40).  
 King, A. H. (1).  
 Kratz, G. D., Flower, A. H. & Coolidge, C. (1) See Aniline.  
 Murrill, P. I. (5).  
 Peachey, S. J. (2) Formaldehyde condensation products of aniline and its homologs. R-100, S-10, Accel-1.0. Cure 40 min./140° C.  
 Pickles, S. S. (1).  
 Rosenbaum, J. L. (1).  
 Rubber Service Laboratories. (1) Methylene aniline prevents scorching by thiocarbanilide when used in conjunction with it.  
 Twiss, D. F. (12).  
 Twiss, D. F. & Brazier, S. A. (1).  
 Weber, L. E. (9) A desirable accel. Gives white stocks which later discolor. Gives off HCHO during factory operations. Free from scorching or toxic effect. Use 1½ or 2% on the R. content. ZnO is desirable.  
 Williams, C. S. (1) Tables of compounding and testing data.

**Methylene Bases.**

- Bayer & Co. (6) Methylene bases as accels. of vulc.

**Methylene Blue.**

- Anon. (255).  
 Bayles, E. A. (1) A retarder of the vulc. of R. See Dinitrosophenol.  
 Gaisman, L. & Rosenbaum, J. L. (1) A combined dye and accel.  
 King, A. H. (1).  
 Meeus, E. de. (1) Used the dye base as an accel.  
 Peachey, S. J. (11) Retards the vulc. process.

**Methylene Diamines.**

- Bayer & Co. (6) Methylene diamine derivatives as accels. of vulc.

**Methylene Diphenylamine.**

- Bastide, J. (1) An accel.

**Methylene Diphenyldiamine.**

- Bastide, J. (1) Uses this accel. with zinc and iron oxides.  
 Bedford, C. W. (1) & (4) The sulfur reaction product of this accel. is formed before compounding with R.  
 Bedford, C. W. & Scott, W. (1) This accel. reacts with S at curing temp. to form thiocarbanilide and other thiourea derivatives.  
 Cranor, D. F. (1)  
 Murrill, P. I. (5).  
 Peachey, S. J. (2) Formaldehyde condensation products of aniline and its homologues as accels.

**Methylene-p-toluidine.**

- Naylor, R. B. (1) An accel. of Vulc.

**Micro-organisms.** See Enzymes.**Mineral Rubber.**

- Bronde, W. T. (1) Elastic bitumen or Mineral caoutchouc originally found in Derbyshire by Dr. Lester. See Phil. Trans. (1673) and J. Phys. 31, 312.  
 North, C. O. (3) Compounding data and effect on the physical properties of vulc. R.  
 Pickles, S. S. (3) Prevents oxidation by decreasing the porosity of R.  
 Smith, A. H. & Epstein, S. W. (1) Mineral rubber and S stirred together at 200° C. react vigorously with evolution of H<sub>2</sub>S.

**Mold.** See Enzymes.**Molecular Weight of Rubber.**

- Gladstone, J. H. & Hibbert, W. (2) High molecular weight (2000).  
 Hinrichsen, F. W. & Kindscher, E. (3) Mol. wt. 3173.

**Molybdenum Blue.**

- Lascelles-Scott, W. (34) A good pigment not injured by R. or exposure to light.

**Molybdenum Dithiocarbamates.**

- Molony, S. B. & Nikaido, Y. (1) & (2) See Dithiocarbamates.



**Molybdenum Sesquioxide.**

Ditmar, R. (62) A weak accel.  
 King, A. H. (1) (2) A negative accel.  
 in amounts over 10%.

**Molybdic Acid.**

Eaton, B. J. (23) See Tannin.

**Monophenylguanidine.** See Diphenylguanidine.

Kratz, G. D., Flower, A. H. & Coolidge, C. (1) Mentioned as an accel.

**Monopiperidylurea.**

Bayer & Co. (6) An accel.

**Naphthalene.**

Anon. (193) Naphthalene increases the preserving action of  $\text{NH}_3$  on latex.  
 See Latex-Preservatives.

Colman, H. G. & Smith, J. F. (1)  
 Very readily absorbed by R.

Hinrichsen, F. W. & Stern, R. (1)  
 Vulc. of R. in solution in naphthalene.  
 Kletzinsky, V. (1) (2) R. easily swells  
 and dissolves in hot naphthalene.

Mowbray, G. M. (1) Properties and  
 ageing of R. are improved by mixing  
 naphthalene into it.

Rutgers Werke. (1) Naphthalene and  
 its derivatives are used in place of  
 wax, fats, or oils as an aid in mixing.  
 Paraffin containing compounds be-  
 come porous during cure, those con-  
 taining naphthalene do not.

**Naphthalenediamine.**

Anon. (84) An accel.

Bayer & Co. (19) Mentioned. (41)  
 See Ageing-Tackiness.

Ditmar, R. (62) Gives rapid accelera-  
 tion.

Dubosc, A. (30).

Eaton, B. J. (8).

King, A. H. (1).

**Naphthenates.**

Cherchefskey, N. (1) Metallic naph-  
 thenates alone or in mixture with  
 naphthenic acid glycerides are mixed  
 into natural or vulcanized R. Naph-  
 thenic acids may replace the acid  
 glyceride.

**Naphthol (alpha and beta).**

Anon. (247) Has no influence on Vulc.  
 Badische Co. (1) 1% alpha or beta  
 naphthol increases the ageing quali-  
 ties of Vulc. R. See Ageing.

Bayer & Co. (41) See Ageing-Tacki-  
 ness.

Ephraim, J. (1) Tackiness in synth. R.  
 removed by heating with S.,  $\text{MgO}$   
 and aldehyde resin or beta naphthol  
 at  $135^\circ \text{C}$ . for 20-45 min.

General Rubber Co. (1) Treatment of  
 R. coagulum with solution of beta  
 naphthol or homologues to insolubi-  
 lize the nitrogenous material. See  
 Latex-Coagulation. (2) (5) Treat-  
 ment of latex with beta-naphthol to  
 insolubilize the nitrogenous material.  
 See Latex Preservatives. (3) beta-  
 naphthol prevents bacterial action in  
 R. coagulum. See Latex-Coagulation,  
 Latex-Preservatives.

**Naphthyl Amines (alpha and beta).**

Anon. (84).

Bayer & Co. (19).

Blanc, M. le & Kröger, M. (1) See  
 Viscosity.

Boggs, C. R. (1) & (3) Beta-naphthyl-  
 amine as an accel. (4) Beta-naph-  
 thylamine as an accel. in vulc. by  
 Selenium.

Cadwell, S. M. (3) See Aldehyde-  
 Amines.

Ditmar, R. (62) Beta-naphthylamine  
 acts like anthraquinone as an accel.

Dubosc, A. (40).

Hasselt, J. F. B. van. (1) See p-Nitro-  
 sodimethylaniline.

Kratz, G. D., Flower, A. H. & Coolidge,  
 C. (1) Beta-naphthylamine is twice  
 as active as the alpha isomer.

Murrill, P. I. (5).

Ostromuiskii, I. (21) A preserva-  
 tive for R. cured with nitro com-  
 pounds. (25) See Dinitrobenzene.

Ricard, E. (2).

Twiss, D. F. & Brazier, S. A. (1).

**Narcotine.**

Blanc, M. le & Kröger, M. (1) See  
 Peachey Process.

**Natural Accelerators.** See Maturation,  
Protein, Resins, Variability.

Anon. (266).

Beadle, C. & Stevens, H. P. (8) Pon-  
 tianac and Hevea resins are accels.  
 Acetone extraction retards the cure  
 and gives inferior quality if cured  
 without inorganic accels. (9) Pro-  
 teins of R. which are insoluble in  
 acetone and benzene are accels. Ni-

- trogen free R. does not vulcanize with S at the usual temp. Smoked Sheet is recommended for preparing nitrogen free R. The proteins, unbroken by milling or crepeing settle out easily. (10).
- Bernstein, G. (4) Influence of the insoluble constituents of R.
- Boggs, C. R. (3) The natural impurities in the best wild rubbers act as accels.
- Ditmar, R. (14). (18). (19) There is no relation between resin content and rate of cure.
- Ditmar, R. & Wagner, A. (1).
- Dubosc, A. (7) Rôle of resins, proteins and metallic oxides in vulc. (9) Resins vulcanize by producing  $H_2S$ . (10) Agrees with L. E. Weber (3). (25) The decomposition products of R. proteins are amino compounds. (30) Fermented R. proteins heated with S at  $135^\circ$  C. form  $H_2S$  and HSCN. Jelutong resins heated with S give  $H_2S$  and acetylene.
- Eaton, B. J. (5). (6) Soaking freshly prepared slab in alkali solution gives a faster curing R. (16) Excessive crepeing washes out part of the natural accelerator. (17). (18) Protein of R. is liable to change with formation of some substances which act as accels. of vulc. (20) During washing and crepeing little or none of the natural accels. are lost. (21) Decomposition of proteins during maturation gives increase in rate of cure due to formation of nitrogenous bases. Protein from latex when decomposed and added to R. gives increased rate of cure. Tetramethylene diamine (putrescine) which is an accel. is suggested as one of the bases formed during protein decomposition. (26) See Slab Rubber. (32) Natural accels. in slab R. and Hopkinson's evaporated R. Slab R. contains not only vulc. accels. formed by maturation but also those present in the latex and retained in the coagulum. Hopkinson R. has a neutral or alkaline character as opposed to the acid reaction of ordinary rubber.
- Eaton, B. J. & Day, F. W. F. (1).
- Eaton, B. J. & Grantham, J. (1). (2) The curing power of plantation R. is not a function of the nitrogen content. (4) Natural accels. are decomposition products of R. proteins by fermentation or chemical action. Amino acids are the natural accels. (5) Isolation of a nitrogenous and a non-nitrogenous accel. from latex serum.
- Eaton, B. J., Grantham, J. & Day, F. W. F. (1) Summary of their work to 1918.
- Editorial. (3).
- Frank, F. & Marekwald, E. (5) True proteins found in R. and latex. They give amino acids on hydrolysis.
- Gorter, K. (11) The serum from acetic acid coagulum gives off ammonia when evaporated with  $MgO$ . See Amyl Amine.
- Grantham, J. (1).
- Hillen, G. H. (1).
- Hinrichsen, F. W. (2) Resins of various rubbers.
- Hinrichsen, F. W. & Marcossou, J. (1).
- Ingle, H. (1).
- Jacobson, F. (1) Bibliography and data on R. resins.
- King, A. H. (1) Discussion.
- Kratz, G. D. & Flower, A. H. (3) R. proteins do not respond to magnesia the same as the acetone extract.  $MgO$  activates the natural R. nitrogen. The amount of  $MgO$  which will function as an accel. is limited by the amount of nitrogenous material present in the R.
- Martin, G. & Elliott, F. L. (1) Crepe R. resins have little effect on the rate of combination of S. Resins from sheet R. are mild in action while slab R. resins are strong accels.
- Meyer, Lothar. (1) R. deprived of its resins cannot be vulcanized.
- Peachey, S. J. & Leon, M. (1) Presence of normal percent of natural resins retards the oxidation of R.
- Pickles, S. S. (1) Lime and  $MgO$  set free volatile bases from R. proteins.
- Porritt, B. D. (1) p. 5. Resins exert an influence on the vulc. process.
- Rosenbaum, J. L. (1) Natural accels. extracted from natural R. and added to synth. R.
- Rossem, A. van. (3) & (4). (6) Synthetic accels. are preferable to the natural accels. due to lack of variation. There is no relation between

- the nitrogen content of R. and its curing power.
- Rossem, A. van & Dekker, P. (1).
- Schidrowitz, P. (30) Hevea latex contains natural accels. Maturation produces a further active type of accel.
- Schidrowitz, P. & Goldsbrough, H. A. (8) Smoked sheets cure faster than first latex crepe.
- Schmitz, W. C. (1) (3) See Protein.
- Skellon, H. (1) Extraction of the R. resin increases the strength of the R. and decreases the coeff. of vulc. but the R. ages poorly.
- Spence, D. (21) The natural accels. function at temperatures of 60° C. and higher. (28) R. resins are accels.
- Spence, D. & Kratz, G. D. (1) R. nitrogen is not entirely of protein origin. The acetone extract contains bodies having well defined alkaloidal characteristics.
- Spence, D. & Young, J. (2) Effect of R. resins on coefficient of vulc.
- Stevens, H. P. (2) Nitrogen free R. will not vulcanize. Peptones, starch and casein act as accels. Absence of protein will not give a normal vulcanizate. PbO works as well in absence of proteins. (5) Removal of resins retards vulc. The vulc. R. ages poorly. (13) 1.67% dried serum decreases time of cure 80%. In protein free R. the accelerating effect was much greater. Quebrachite retards the rate of cure of protein free R. Decomposed proteins as accels. There is no relation between the percent of nitrogen and the vulcanizing properties of plantation R. (15). (17). (21). (27) See Slab Rubber. (42) See Maturation. (60) See Variability. (54) A natural accel. from decomposition of the Protein in latex is present in slab R. (60) The rapid vulc. of evaporated latex is due only to a small degree to putrefactive bases. (61) The surface of putrefying coagulum is alkaline while the interior is acid. Dried latex shows more rapid curing. This is not due to putrefactive bases. Surface changes are unimportant. The increased rate of cure, if caused by micro-organisms, must be caused by the action of the anaerobic type
- (73) Effect of resins, proteins and putrefactive base.
- Tschirch, A. & Schmitz, W. C. (1) Isolation of the nitrogenous bodies in R.
- Tuttle, J. B. (1) ZnO should be used in quality tests on plantation rubbers.
- Twiss, D. F. (9) See Variability.
- Twiss, D. F. & Brazier, S. A. (1) Fermentation of wet coagulum changes proteins to accels.
- deVries, O. (14) Natural accels. have less effect on Sc for a fixed cure than artificial accels. (19) Accels. formed during maturation are not extracted by water. Soaking in water, extracts serum substances and decreases the rate of cure. Further soaking (24-48 hrs.) increases the rate of cure. (24) p. 254. The residue obtained by evaporating the latex serum accelerates vulc. (28) Nitrogenous bodies, amines or amino acids which play a part in building up or decomposition of proteins are mainly responsible for differences in rate of cure. Natural accels. are present in the same proportion over the whole tapping area. See Sulfur-Coefficient of Vulcanization.
- Weber, L. E. (2) Litharge will not cure in the absence of rubber resins. (3) The lowering of the acetone extract by metallic oxides is attributed to the formation of metallic resinates.
- Whitby, G. S. (4) Discussion of Eaton, B. J. & Grantham, J. (4). (10) The chemical nature of R. resins.
- Whitby, G. S. & Dolid, J. (1).
- Nickel Oxide.**
- Ditmar, R. (62) A powerful negative accel.
- King, A. H. (1) (5) A negative catalyst. Will entirely prevent the vulc. of R.
- Nicotine.**
- Blanc, M. le & Krüger, M. (1) Accelerates the formation of S in the Peachey Process.
- Muntz, W. E. (1) Impregnation of fabric with nicotine as an ant-acid and later coats the fabric with R. and vulcanizes. No mention of an effect on time of cure.

- Ostwald, Wo. & Ostwald, Wa. (1) Painted on R. goods to prevent deterioration.
- m-Nitraniline.**  
Cadwell, S. M. (3) See Aldehyde-Amines.
- p-Nitraniline.**  
Cadwell, S. M. (3) See Aldehyde-Amines.  
Dubosc, A. (40) p-Nitraniline mentioned as an accel.
- Nitrate of Hexamethylenetetramine.**  
Dubosc, A. (47) Reactions of the acid nitrate and neutral nitrate during vulc. Acid Nitrate:  $7S + C_6H_{12}N_4 \cdot N_2O_5 \cdot H = 6(CSNH) + 3N_2O + H_2S$ . Neutral Nitrate:  $8S + C_6H_{12}N_4 \cdot N_2O_5 \cdot H = 5(CSNH) + 3H_2O + H_2S + CS_2$ .
- Nitric Acid.**  
Achard, F. (1)  $HNO_3$  colors caoutchouc yellow, forming  $N_2$ ,  $CO_2$ ,  $HCN$ , oxalic acid and a fatty body. Fuming  $HNO_3$ , 6 pts., dissolves 1 pt. caoutchouc from which water throws down a yellow precipitate which is soluble in acids, alkalis and alcohol and inflammable at  $100^\circ C$ . (1866).  
Allen, (1) p. 156. Action on gutta percha.  
Austin, P. T. (1) Rubber ignited in air burns with a white smoky flame, when introduced into gaseous nitric acid the flame loses its luminosity. R. in gaseous  $HNO_3$  soon evolves a gas which ignites and burns with a flame having a bright core and pale halo.  
Blossom, T. M. (1)  $HNO_3$  on R. gives  $CO_2$ , N,  $NO_2$  and oxalic acid.  
Camille, A. (5) Action on R.  
Ditmar, R. (1) Conc.  $HNO_3$  on R. gives a nitro derivative of R. 22% yield of Nitrosate of the formula  $C_{10}H_{12}N_2O_6$ . (4) Fuming  $HNO_3$  on R. forms 3:6 or 3:5 dinitro dihydro-cuminic acid. Soluble in glacial acetic acid, acetone and quinoline. Alkali salts are red, amorphous substances, soluble in water. Methyl ester,  $C_9H_{11}O_4N_2CO_2CH_3$  is a red powder. Acetyl anhydride,  $C_9H_{11}O_4N_2CO_2COCH_3$  is an orange red powder. m.p.  $72^\circ C$ . The dinitro compound is reduced to diamino dihydro-p-cuminic acid, a dark brown powder, by heating with  $SnCl_2$  and  $HCl$ . (22) Action on balata. See Balata.  
Dubosc, A. & Luttringer, A. (1) p. 177.  
Eaton, B. J. (3) Study of range over which coagulation of latex is complete or incomplete with  $HNO_3$ .  
Fourcroy, A. F. (2)  $HNO_3$  on R. gives  $N_2$ ,  $CO_2$ ,  $HCN$  and oxalic acid.  
Fourcroy, A. F. & Nicholson, W. (1).  
Geer, W. C. (5) p. 22. Chas. Good-year treated R. with  $HNO_3$  in 1837 and nearly suffocated from the fumes.  
Goodyear, Chas. (3) Vulc. of R. by  $HNO_3$ . (5) Wash the surface of R. articles (unvulcanized) with concentrated  $HNO_3$  or a concentrated solution of  $Cu(NO_3)_2$  or  $Bi(NO_3)_3$ , wash with water or bleaching powder and dry.  
Gottlob, K. O. (2) Action on R.  
Hare, R. (1) Fused R. inflames in conc.  $HNO_3$ .  
Harries, C. (2) Action of  $HNO_3$  on R. nitrosite. See Nitrosite.  $HNO_3$  on R. gives formic, oxalic and other acids. (25) Repeated Ditmar's work with substantially the same results. In the mother liquor of the dinitro compound he found oxalic acid and a yellow oil having acidic properties. This oil gave a silver salt,  $C_8H_5NO_3$ -Ag. (31) p. 48.  
Heinzerling, C. (1) p. 29. Conc.  $HNO_3$  and a mixture of  $H_2SO_4$  and  $HNO_3$  attack crude R.  $HNO_3$  colors it yellow and decomposes it with formation of  $N_2CO_2$ , oxalic acid and an aliphatic compound. On boiling it dissolves with formation of comphe-sinic acid.  
Henriques, R. (1) Fuming  $HNO_3$  attacks all varieties of R. and dissolves them. (4) Suggested the use of fuming  $HNO_3$  in R. analysis.  
Herbst, E. & Stern, R. (1).  
Jones, H. W. (1) Used as a solvent for vulcanized rubbers.  
Koller, P. (1) 6 pts. fuming  $HNO_3$  on 1 pt. R. gives a solution which precipitates out on dilution. Action of acids and alkalis on R.  
Leonhardi, J. G. (1) Conc.  $HNO_3$  makes R. yellow and friable. Fuming  $HNO_3$  dissolves R. and on dilution gives a yellow precipitate which

- inflames if heated above 100° C. (1871).
- Marchwald, E. & Frank, F. (6) p. 41. HNO<sub>3</sub> on latex precipitates a white albuminous compound identical with Faraday's albumin.
- Matthews, R. (1) Boiling aqueous HNO<sub>3</sub> changes R. to a brittle porous mass (1805).
- Morgan, S. (1) p. 216 & 233. HNO<sub>3</sub> gives good coagulation of latex but a slow curing R.
- Nicholson, W. (1) HNO<sub>3</sub> on R. evolves nitrous oxide. Oxalic acid is found in the residue. (1808).
- Obach, E. F. A. (1) Dilute HNO<sub>3</sub> (1:20) does not attack gutta percha. Strong HNO<sub>3</sub> completely oxidizes it.
- Parepa, M. C. D. (1) Conc. HNO<sub>3</sub> violently attacks caoutchouc destroying the isoprene and forming carbonic and oxalic acids and water. It attacks caoutchine, oxidizing and nitrating it at the same time with formation of dinitro-dimethyl-benzoic acid. Considers caoutchine as a hydrogenation product of dimethyl ethylbenzene which gives the same product as he obtained from R. Obtained 25% yield of yellow product. Prepared the silver salt and a sulfonic acid derivative of the nitro compound. Violence of HNO<sub>3</sub> action on R. is due to ease with which isoprene is oxidized to oxalic acid; the caoutchine gives the yellow nitro compound.
- Ramsay, Chick & Collingridge. (1) Action on gutta percha.
- Roxborough, W. (1) When digested for 12 hours HNO<sub>3</sub> converts R. into a soft yellow inelastic mass which becomes friable on standing.
- Schidrowitz, P. (6) p. 216. Strong HNO<sub>3</sub> oxidizes R.
- Schwanert. (1) R. dissolves in HNO<sub>3</sub> (sp. gr. 1.35) on boiling, forming camphresinic (camphretic) acid and a resin which can be precipitated with water. Lead salt of the acid was prepared.
- Seeligmann, Torrilhon & Falconnet. (1) p. 132. Action of HNO<sub>3</sub> on R. p. 117. Cold conc. HNO<sub>3</sub> does not attack the globules of Hevea latex but it decomposes the serum in which it produces a gelatinous precipitate.
- Spence, D., Galletly, J. C. & Scott, J. H. (1) Action on R. tetrabromide.
- Terry, H. L. (1) Dilute HNO<sub>3</sub> on R. gives a brittle yellow powder. (2) The ultimate action of HNO<sub>3</sub> is to form oxalic and carbonic acids. An intermediate nitro compound is formed which is soluble in caustic alkali. (3) Dil. HNO<sub>3</sub> in 6 weeks on R. gives a yellow brittle powder which has explosive properties. It may be a mixture of an oxidized and nitrated substance. (5) Fuming, concentrated or dilute HNO<sub>3</sub> give the same compound with R. Action of HNO<sub>3</sub> on the oily distillation products of R. and on the halogen derivatives of R. (15) p. 72. HNO<sub>3</sub> even in very dilute solution attacks R. with formation of nitro resinous compounds. If oxidation is carried far enough, all of the R. is converted to oxalic and carbonic acids.
- Thenard, L. J. (1).
- Thomson, W. & Lewis, F. (1) HNO<sub>3</sub> acts harmfully on R. See Hydrochloric acid.
- Torrey, J. (1) Colorimetric determination of R. Conc. HNO<sub>3</sub> on R. gives a material soluble in caustic alkalies. The tint of this solution is compared to a standard made of pure R.
- Trommsdorf, J. B. (1) Fuming HNO<sub>3</sub> on R. Acid was diluted with water to avoid fire. Water precipitated a yellow inelastic product, insoluble in alcohol.
- deVries, O. (24) p. 185. Like HCl it has the property of leaving latex uncoagulated when added in a certain, not too large, amount.
- Whitby, G. S. (5) Study of range over which coagulation of latex is complete or incomplete with HNO<sub>3</sub>.
- Wiesner, J. (1) See Balata.

#### Nitroanthracene.

Gibbons, W. A. (1) Used with PbO as a vulc. agent of R.

#### Nitrobenzene.

See m-Dinitrobenzene.

Buntschoten, E. (1) Review of the work of Ostromuiskii.

Ostromuiskii, I. (15) Vulc. with nitro compounds has nothing to do with their ability to give additive

reactions with double bonds. Vulc. takes place by loss of oxygen from the nitro group. (19) & (25) See Dinitrobenzene. (30) Vulc. by the combined action of nitro compounds, metallic oxides and S.

Stevens, H. P. (14) Repetition of the work of Ostromuiskii.

Weber, C. O. (7) Use of nitrobenzene in R. analysis and its effect on the R.

#### Nitrocellulose.

Germain, P. (1) A vulcanizing agent for R.

#### Nitro Colors.

Ostromuiskii, I. (25) Vulc. of R. with nitro colors without S.

#### Nitrocresol.

Compagnie Parisienne des Tissus Caoutchouc. (1) R-100, S-10, nitrocresol-0.5. Cure 12 min./140° C. Also R-100, S-40, nitrocresol-1.0. Cure 2 hrs./140° C. to ebonite. PbO is not necessary and goods of all colors may be made.

#### Nitrocyclohexane.

Ostromuiskii, I. (25) See m-Dinitrobenzene.

#### Nitrogen. See Gases.

Eaton, B. J. & Day, F. W. F. (1) Nitrogen content calculated to dry coagulum decreased from 0.78% to 0.23% after standing for 6 weeks.

Edwards, J. D. & Pickering, S. F. (1) Permeability through R.

Grantham, J. (1) Smoked slab vulcanizes more rapidly than smoked sheet. Both contain same amount of N<sub>2</sub>. As nitrogen content decreases in unsmoked sheet the rate of cure increases. Smoked slab contains the same % of N<sub>2</sub> and still rate of cure increases. Loss of N<sub>2</sub> does not accelerate vulc.

#### Nitrogen Peroxide. See Nitrosites.

#### Nitrogen Sulfide.

Romani, E. (4) N<sub>2</sub>S<sub>2</sub> formed by S<sub>2</sub>Cl<sub>2</sub> on NH<sub>3</sub> will vulcanize R. without the aid of free S. It is also a strong catalyst.

#### Nitrogen Thiobromide (Thiodide).

See Phosphorous Thiobromide.

#### Nitronaphthalenes.

Ostromuiskii, I. (25) See m-Dinitrobenzene.

#### Nitronaphthol.

#### Nitrophenol.

leRoy, G. A. (1) See Phosphorous Thiobromide.

#### Nitrosamines.

Peachey, S. J. (7) Although nitrosamines are isomeric with the nitroso accels. they have no effect on the vulc. of R.

#### Nitrosites.

#### Nitrogen oxides.

#### Nitrous Acid.

Alexander, P. (1) Nitrogen peroxide reaction product is precipitated in a 10% solution of NH<sub>4</sub>Cl to obtain a good solid product. (3) Nitrogen peroxide on a solution of R. does not give a product of the composition, C<sub>10</sub>H<sub>16</sub>O<sub>4</sub>N<sub>2</sub>, as described by C. O. Weber. It closely resembles Nitrosite "C." (4) Nitrous gases on R. give a product having the formula C<sub>8</sub>H<sub>12</sub>O<sub>6</sub>N<sub>2</sub> and is not identical with Nitrosite "C." One carbon is eliminated as CO<sub>2</sub>. Decomposes at 90-110° C. (5) Contrary to R. Ditmar (33) reclaimed R. forms a nitrosite. (8) Tetrabromide and nitrosite derivatives of vulc. R. contain all of the combined S. If the sulfur were only adsorbed it should not be quantitatively precipitated from solutions in which it is soluble. (9) Evidence for nitrosite of formula C<sub>8</sub>H<sub>12</sub>O<sub>6</sub>N<sub>2</sub> and evolution of CO<sub>2</sub>.

Blossom, T. M. (1) Nitrous vapors act rapidly on R.

Camille, A. (5) Nitrous acid vapors attack R. at all temperatures.

Caspari, W. A. (1) Nitrogen peroxide on gutta percha and balata gives buff colored powders. They become pasty at 120° C. Soluble in conc. H<sub>2</sub>SO<sub>4</sub>. They reduce Fehling's solution.

Dieterich, K. (1) Weber's dinitro method gives higher results than Harries' nitrosite method. Fendler's method determines rubber hydrocarbon, while the nitrosite determines the total rubber.

- Ditmar, R. (33) Reclaimed R. forms no nitrosite.
- Dubosc, A. & Luttringer, A. (1) p. 174 to 281, 201. Review.
- Eduardoff, F. (2) Action of nitrous gases on latex.
- Esch, W. (1) Application of nitrosates in rubber analysis.
- Fendler, G. (2) & (3) Harries' and Weber's methods give high results. Certain R. resins give compounds with nitrous acid which are soluble in acetone and insoluble in benzene. (4) Resins do not interfere in the Nitrosite method of analysis.
- Fonrobert, E. & Harries, C. (1) Discussion of the literature.
- Gottlob, K. O. (2) Pure or natural R. treated with nitrous acid containing varying amounts of  $N_2O_4$  gives nitrosites differing from each other but which can all be referred back to Harries' nitrosite "C." Evidence for P. Alexander's nitrosate is insufficient. (4) Exact duplication of C. Harries' directions will give Nitrosite "C." Otherwise a mixture of nitrosated and oxidation products are obtained.
- Hancock, C. (1) Vapor cures with gases from metals and  $HNO_3$ .  $NO_2$  and  $ZnCl_2$  used to improve the quality of R. or gutta percha.
- Harries, C. (1) Nitrosite or nitrosate,  $C_{10}H_{16}N_{10}O_{14}$ , obtained by action of nitrous acid on crude R. in solution of light petroleum. (2) Preparation of nitrosite of R. with excess nitrous acid. Effect of using dry gas. Nitrosite "b,"  $(C_{10}H_{16}N_8O_8)_2$  was obtained. Nitric acid on R. nitrosite gives 25% of a compound  $C_{10}H_{16}N_8O_{14}$ , the remainder is oxidized to oxalic and an aliphatic nitro acid. Nitrosite "b" is oxidized by alkaline permanganate to a mixture of oxalic, succinic and butyric acids. (3) Preparation of Nitrosite "C,"  $(C_{10}H_{16}N_8O_7)_2$ , without exclusion of moisture by passing  $N_2O_4$  into R. solution. This is the only nitrosite that rubber gives. Decomposes  $158^{\circ}$ - $162^{\circ}$  C. Nitrosite "b" is an oxidation product of Nitrosite "C" due to nitrosyl chloride which is formed when the gas is dried over  $CaCl_2$  and  $P_2O_5$ . (4) Rubbers from different sources all gave the same nitrosite,  $C_{10}H_{16}N_8O_7$ . (8) Nitrogen peroxide does not give as uniform a product with R. as nitrous anhydride. The composition closely resembles that of Nitrosite "C." (10) Gutta percha gives a nitrosite,  $C_{10}H_{16}N_8O_7$ , similar to R. (11) Action of nitrous acid and nitrogen dioxide on R. See Ozone. (12) The difference between Harries' and Alexander's nitrosite is due to preparation of the nitrous gases and purification of the product. (13) Purification of nitrosite. (31) p. 26-48. Nitrosites of R. p. 118. Of gutta percha.
- Harries, C. & Rimpel, H. (1) See Tetra bromide.
- Korneck, O. (1) Harries' nitrosite method is not accurate because the resin and protein nitrosites are weighed as R. nitrosite and secondly because the gases and solvents which adhere to the product are also weighed.
- Last. (1) R. recovered from the nitrosite. The oxidation tendency of 12 samples.
- Parkes, A. (1) Vapor cures with oxides of nitrogen and with liquid  $S_2Cl_2$ .
- Pontio, M. (1) Analysis of R. by the nitrosite method.
- Terry, H. L. (3) The monoxide of nitrogen has no action on R. The dioxide has a slight action while the higher oxides react readily. (5) Nitrogen oxides give a yellow compound with R.
- Weber, C. O. (15) Nitrosite,  $C_{10}H_{16}N_8O_7$ , obtained by passing absolutely dry nitrous acid into a benzene solution of R. Nitrosate,  $C_{10}H_{16}N_8O_8$ , obtained by passing  $N_2O_4$  into a benzene solution of R. m.p.  $112^{\circ}$  C. Balata and gutta percha also give this product. Sodium and silver salts were prepared. Solubility in solvents. (15) & (51) Nitrogen peroxide on a benzene solution of R. gives an amorphous product, decomposing at  $112^{\circ}$  C. (55)  $N_2O_4$  adds to vulc. R. without disturbing the combined S.  $(C_{10}H_{16})_n S(N_2O_4)_n$  is formed. Soluble in acetone.
- Nitrosobenzene.**
- Alessandri, L. (1) Nitrosobenzene forms a red yellow compound with R.

- Bruni, G. & Romani, E. (1).  
 Ostromuiskii, I. (15) Will not vulcanize R. like the nitro compounds.  
 Peachey, S. J. (15) R-100, S-10, Nitrosobenzene-0.5. Cure 1 hr./45 lbs. to soft R. R-100, S-40, Nitrosobenzene-0.6. Cure 3 hrs./45 lbs. to hard R. This accel. scorches on the mills and cannot be calendered. (16) R-10, S-1, CS<sub>2</sub>-150, Nitrosobenzene-0.6. This cement sets to a gel in 30 min. at ordinary temp.
- Nitrosocresol.** See Nitrosophenol.
- p-Nitrosodiethylaniline.**  
 Peachey, S. J. (4) An accel.  
 Rosenbaum, J. L. (1).
- p-Nitrosodimethylaniline.**  
 "Accelerene." See Sulfur reaction products of Accelerators.  
 Anon. (84) Does not work well with reclaimed R. Prevents bloom. (125) (255) The theories of E. Seidl and W. Esch for metallic oxides do not apply to this accel.  
 Bedford, C. W. & Sebrell, L. B. (1) Mechanism of action of Nitroso accels. (2) Reacts with H<sub>2</sub>S to give free S but this reaction will not vulcanize a R. cement.  
 Bedford, C. W. & Sibley, R. L. (1) See Thiocarbanilide. (2) The H<sub>2</sub>S reduction product of p-nitrosodimethylaniline described as an accel.  
 Blanc, M. le & Kröger, M. (1) Accelerates the precipitation of S by the Peachey Process. Also effect on vulc. in solution by S and S<sub>2</sub>Cl<sub>2</sub>.  
 Boggs, C. R. (4) Used as an accel. in vulc. with selenium.  
 Brooks, B. T. (1) p. 136.  
 Bruni, G. & Romani, E. (1).  
 Bunschoten, E. (1) Retards the curing of R. without S by nitro compounds.  
 Dannerth, F. (1).  
 Dittmar, R. (62).  
 Dubosc, A. (30) This accel. generates HSCN, SO<sub>2</sub> and H<sub>2</sub>S during vulc. with S. (40). (42) Decomposes during vulc. to HCN and HCNS.  
 Earle, D. (1) Causes severe inflammation of the skin.  
 Endres, H. A. (1) Comparison of several accels.  
 Gaisman, L. (1) Non-poisonous.  
 Gottlob, K. O. (9) Nitroso bodies oxidize the R. and are therefore detrimental.  
 Hasselt, J. F. B. van. (1) Two mols. of this accel. react with 1 mol. of aromatic amines to form double salts which are preferable as accels. The double salts are as active weight for weight as the nitroso compound itself.  
 India Rubber, Gutta Percha & Telegraph Works. (1) Used in a composition for soles, heels, steam joints, etc.  
 Kratz, G. D., Flower, A. H. & Coolidge, C. (1) This accel. is changed to a base during vulc.  
 Murrill, P. I. (5).  
 Peachey, S. J. (4) R-100, S-10, Accel.-0.5. Cure 20 Min./135° to 145° C. for soft R. R-100, S-40, Accel.-0.75 to 1.0. Cure 2 hrs./145° C. to ebonite. (7) Produces very little acceleration with antimony sulfide when little or no free S is present. (8) A portion may remain unchanged in the cured R. (10) Polemical with D. Spence. (11) Tends to stick to back rolls during mixing. Mixing with 20% kieselguhr avoids this difficulty. MgO aids its action. Does not work well with reclaimed R. Very good for ebonite. When heated with R. gives a tarry mass. Causes dermatitis. Persons who perspire freely cannot work with it. (12) Description of the use of Accelerene in soft and hard rubber. 0.5% for soft R. and 0.75% for ebonite are recommended. Reduces bloom. Must be added quickly on the mill or partial vulc. occurs.  
 Pearson, H. C. (1) p. 83.  
 Pickles, S. S. (1).  
 Ricard, E. (2).  
 Rosenbaum, J. L. (1) Cannot be used in white stocks. Subject to decomposition. Does not work well with PbO.  
 Rossem, A. van. (6) Comparison with piperidine and aldehyde ammonia by coefficient of vulc.  
 Scott, W. & Bedford, C. W. (1) Reacts with H<sub>2</sub>S to give p-aminodimethylaniline. With S in the cure it gives H<sub>2</sub>S and SO<sub>2</sub>.  
 Shephard, N. A. & Krall, S. (1) See Hexa.



- Spence, D. (28) Polemical with S. J. Peachey.
- Stevens, H. P. (21) R-100, S-10, Accel.-0.25. Excess coefficient 5.17. R-100, S-10, MgO-1.0. Excess coefficient 4.827.
- Twiss, D. F. (4) R-95, S-5, Accel.-1. Cure 90 Min./40 lbs. Free S-1.5%. Free sulfur without accel.-3.6%. (5) No nitroso accel. approaches the best basic accels. in curing power. (12).
- Twiss, D. F. & Brazier, S. A. (1).
- Weber, L. E. (9) Not popular in the U. S. due to its poisonous properties.
- p-Nitrosodiphenylamine.**  
Anon. (255) An accel.  
Peachey, S. J. (3) & (4) An accel.  
Rosenbaum, J. L. (1).
- Nitrosoguanidine.**  
Dubosc, A. (40) An accel.
- Nitroso-hexamethylenetetramine.**  
Dubosc, A. (40) An accel.
- Nitroso-monoethylaniline.**  
Peachey, S. J. (4) An accel.  
Rosenbaum, J. L. (1).
- Nitroso-monomethylaniline.**  
Peachey, S. J. (4) An accel.  
Rosenbaum, J. L. (1).
- Nitroso-naphthol.**  
Peachey, S. J. (4) Active accel. of vulc. (11).
- Nitrosophenol.** (Nitrosoxytol).  
Bedford, C. W. & Sebrell, L. B. (1) A cement containing nitrosophenol, S, CS<sub>2</sub>, and ZnO will gel at room temp. if treated with H<sub>2</sub>S. Mechanism of action of nitroso accels.  
Bruni, G. & Romani, E. (1).  
Peachey, S. J. (4). (5) R-100, S-10, Nitroso phenol-1. Cure at 135°-145° C. Reduces time of cure from 1 hr. to 30 or 35 min. (7). (11).  
Stevens, H. P. (42) Mechanism of action of nitroso accels.
- Nitrosyl Chloride.**  
Dubosc, A. & Luttringer, A. (1) p. 52. No NOCl derivative of R. has been prepared.  
Fonrobert, E. & Harries, C. (1) p. 147. NOCl passed into a benzene solution of R. forms a bluish white precipitate, which contains the calculated amount of Cl and N but it seems to be highly oxidized due to the presence of nitrous acid.  
Gottlob, K. O. (6) p. 7. NOCl reacts with R.  
Hinrichsen, F. W. & Memmler, K. (1) p. 52. NOCl does not give a homogeneous product with R.  
Porritt, B. D. (1) p. 35.  
Tassilly, E. (1) p. 314.  
Weber, C. O. (15) NOCl added to a R. solution sets the latter to a gel but the rubber seems to be unchanged. (61) p. 4. Apparently no NOCl derivative of R. can be prepared.
- Nitrotoluenes.**  
Ostromuiskenskii, I. (13) Vulc. with PbO and mono-, di-, or trinitrotoluene. See Nitrobenzene.  
leRoy, G. A. (1) See Phosphorous Thiobromide.
- Nitrous Acid.** See Nitrosites.
- Nitrous Anhydride.** See Nitrosites.
- Nitrous Oxide.** See Gases.
- "Normal" Rubber.** See Dimethylbutadiene-rubber.
- Ocotillo gum.**  
Snyder, E. W. (1) 1% Ocotillo gum in R. improves its wearing qualities in shoes, etc.
- Odor.**  
Breuil, P. (6) See Zinc Chloride.  
Frank, F., Marckwald, E. & Liebschutz, J. (1) See Resins.  
Schnurpeil, M. (1) Odor of R. goods removed by treating with air at 70-75° C. NH<sub>3</sub> not recommended. MgO is useful.  
Schulze, E. (5) Use of purified naphtha is best means of avoiding odors. Discussion of natural odors of R.  
Shirai, S., Tanaka, S. & Yosikawa, B. (1) Odorless R. is made by vulcanizing with sodium carbonate and soda ash instead of S.  
Terry, H. L. (12) Odor of waterproof goods is more often due to the naphtha, CS<sub>2</sub>, or oils than to the R. May also be due to oxidation of albumins.  
Weber, C. O. (16) Removal of odor from R. goods. (38) Cause of odor in rubberized goods.

**Oils.**

- Bell, P. C. (4) (5) Action of vegetable oils, mineral oils and fats on R.  
 Burghardt, C. A. (1) Certain oils act harmfully on R.  
 Dannerth, F. (1) Physical and chemical properties of oils, fats, waxes and resins used in the R. industry. (4) Mineral oils, fats and waxes used in R. compounds.  
 Heinzerling, C. & Pahl, W. (1) Destructive action of oils on R. is checked by addition of PbO and ZnO.  
 Holde, D. (1) Mineral oils are sometimes adulterated with R. to increase their viscosity and lubricity.  
 Jolles, A. & Wallenstein, F. (1) The fat from leather decomposes R.  
 Lascelles-Scott, W. (10) Eucalyptus oil is objectionable in R. due to ozonizing action. R. containing oil of citronella deteriorated worse than without it.  
 Terry, H. L. (9) Action of oils on R.  
 Thomson, W. (1) Certain oils placed on R. cause rapid oxidation and depolymerization to a jelly like mass.  
 Weber, C. O. (35) Palm oil preferred to linseed, colza or ricinus oil because it has less tendency to oxidize. Free fatty acids of palm oil probably combine with PbO or ZnO and thus act favorably on the R.  
 Wiesner, J. (1) p. 386. Deterioration of R. is accelerated by applying olive or palm oil on the R.

**Oleic Acid.** See Acids—Organic.

- Weber, L. E. (9) Oleic and stearic acids as well as rancid castor oil are accels. of vulc. Oleic acid is the "original organic accelerator," discovered in the laboratory of C. O. Weber in 1904.

**Organic Accelerators.** See Accelerators.

**Oxalic Acid.** See Latex-Coagulants and Nitric Acid.

- Eaton, B. J., Grantham, J. & Day, F. W. F. (1) Used as a coagulant it gives a R. resembling that made with acetic acid.  
 Morgan, S. (1) p. 216 & 224. Use as a latex coagulant.  
 Nicholson, W. (1) Formed by action of HNO<sub>3</sub> on R. (1808).

**Oxidase.** See Enzymes.

**Oxidation.** See Ageing-Oxidation.

**Oxybutyl-thiocarbonic-disulfide.**

- Cadwell, S. M. (1) (5) (6) See Xanthates.

**Oxyfurfuraniline.**

- Dubosc, A. (54) An accel.  
 Ricard, E. (2) See Furfural.

**Oxygen.** See Ageing-Oxidation.

- Edwards, J. D. & Pickering, S. F. (1) Permeability of R. to gases.  
 Kaye, F. (1) Oxidation of proteins causes coloration of R.  
 Ostromuiskii, I. (12) Vulc. by atmospheric O<sub>2</sub> activated by moisture. See Light.  
 Venable, C. S. & Fuwa, T. (1) Solubility of O<sub>2</sub> in R.

**Oxygen Compounds in Rubber.**

- Alexander, P. (2) Acetone soluble portion of Pontianac R. contains an oxygen compound C<sub>28</sub>N<sub>4</sub>O.

**Oxyquinoline.**

- Anon. (84) An accel.  
 Ditmar, R. (62).  
 Dubosc, A. (40).  
 Pearson, H. C. (1) p. 86.

**Oxyquinoline Sulfide.**

- Anon. (84) An accel.  
 Ditmar, R. (62) A very energetic accel. Too active.  
 Dubosc, A. (40).  
 King, A. H. (1).  
 Pearson, H. C. (1) p. 86.

**Oxyquinoline Sulfonic Acid.**

- Anon. (84) An accel.  
 Ditmar, R. (62) A good accel. but gives a porous R.  
 Dubosc, A. (40).  
 Pearson, H. C. (1) p. 86.

**Oxysulphochloram.**

- Rodier, P. (1) Vulcanizes R. at 50-60° C. Alkali sulfides are used as aids. Compound is prepared by passing Cl into a cooled mixture of ammoniacal chloride of S and sulfuric monochlorhydrin. m.p. 54° C.

**Ozone.**

**Ozonides.** See Ageing-Oxidation, Ageing-Tackiness, Viscosity, Laevulinic Acid, Laevulinic Aldehyde.

Anon. (237) (241) Ageing of R. goods tested by exposure to  $O_3$ .

Asano, K. (1)  $O_3$  attacks R. at ordinary temp.

Badische Co. (4) Vulc. of R. by heating with the oxonides of R., isoprene or terpenes.

Bayer & Co. (17) (18)  $O_3$  on R. gives laevulinic aldehyde, mono- and dimethyl-succinic-aldehyde and acetyl acetone.

Bolas, T. (2) Even a trace of  $O_3$  will attack R.

Dubosc, A. (5) Discussion of the work of Harries.

Dubosc, A. & Luttringer, A. (1) p. 181 & 205.

Fonrobert, E. & Harries, C. (1) p. 159. Ozonide of gutta percha. p. 152 of R.

Gottlob, K. O. (1) African Rs. differ from Para R. in giving more laevulinic acid than laevulinic aldehyde by reaction with  $O_3$ .

Harries, C. (6) Para R. gives an ozonide  $(C_{10}H_{16}O_8)_x$  which with water gives keto and dialdehydes, laevulinic acid and  $H_2O_2$ . Oxalic acid was not found. (9) Decomposition products of R. ozonides. (10) Action of  $O_3$  on R. and gutta percha. (11) Nitrosites and ozonides of R. which has been regenerated from its ozonide. (18) Theory of the 8 carbon ring from reactions of  $O_3$  on R. (19) Chemical identity of natural and synth. R. proven thru their ozonides. (20) Action of solutions of  $O_3$  on R. (23) (25) Mechanism of the action of  $O_3$  on organic compounds. See Rubber Hydrochloride. (29) Identification of synth. R. in natural R. by ozonizing in the presence of  $CaCO_3$ . (30) Action of  $O_3$  on unsaturated organic compounds. (31) p. 51, 79 & 120.

Harries, C. & Osa, A. S. de. (1)  $O_3$  on unsaturated compounds.

Harries, C. & Weil, R. (1) Action of  $O_3$  on Para R. vs. other unsaturated compounds.

Herbst, E. & Stern, R. (1) Action of  $O_3$  on R.

Lichtenberg, O. (1) Diacetyl propane from R. ozonide. See Rubber Hydrochloride.

Minder, J. (5)  $O_3$  on R.

Morgan, H. W. (1) R-S cements are treated with  $O_3$  prior to vulc.

Obach, E. F. A. (1)  $O_3$  readily attacks R. but has little action on gutta percha.

Olivier, S. C. J. (1) Harries' formula for R. R. ozonide cannot be dried to constant weight. The molecular weight of R. ozonide does not reveal the size of the R. molecule.

Ostromulesskii, I. (11) Terpene ozonides or  $O_3$  itself as vulc. agents. (12) Ultra violet light vulc. R. by the production of  $O_3$ . The best temp. is at 40-80° C. At 120° C. a tacky product results. (17) See Light.

Snelling, W. O. (1) R. treated with  $O_3$  in the presence of water and Cu oleate gives a plastic material.

Thomson, W. (3) Passed  $O_3$  over R. stretched and unstretched. The former perished in a few minutes with the latter still unchanged.

Wright, A. W. (1)  $O_3$  on ebonite generates  $SO_2$  and  $H_2SO_4$ .

**Paladium.**

Thomson, W. & Lewis, F. (1) See Copper.

**Papain.**

Anon. (266) See Latex-Coagulation.

**Paraffine.**

Rossem, A. van. (6) Injurious to vulc. R.

**Peachey Process for Vulcanization by gases.****Hydrogen Sulfide and Sulfur Dioxide.**

American Chemical Society. (6) At the Chicago meeting in 1920, G. D. Kratz exhibited samples of R. cured by the Peachey process in which one-half of the total S was uncombined. C. W. Bedford suggested that the two gases might form trithioozone.

Anon. (90) Possibilities of the Peachey Process. (94) & (302) Peachey process of cold vulc. (297) Peachey Process. (309) "Poured goods" vulcanized by the Peachey process. Vulcanized cements which are still liquid.

- Bedford, C. W. & Sebrell, L. B. (2)  $H_2S$  and  $SO_2$  react in cold benzol to give a form of S which will vulc. a R. cement at room temp. See Trithioozone.
- Blanc, M. le & Kröger, M. (1) Vulc. of R. solutions by the Peachey process with and without the presence of organic accelerators. Quinoline, p-nitrosodimethylaniline, nicotine, piperidine and narcotine. See Viscosity and Colloid Chemistry.
- Dubosc, A. (30) (40) See Vulcanization-theories. (61) Claims priority for the Peachey Process.
- Hutin, A. (4) Comparison of Peachey process with the older methods of vulc.
- Jones, F. (1) Mixtures of R. and celluloid vulcanized by this process. (4) Moulding articles from gels vulc. by the Peachey process.
- Kaye, F. (4) Comments on Peachey Process.
- Peachey, S. J. (9) (20) (21) (26) Vulc. of R. by  $H_2S$  and  $SO_2$ . (14) R. is vulcanized in the cold by alternate treatment with  $SO_2$  and  $H_2S$ , the two gases forming S within the R. Process may be used to vulcanize a R. solution in benzene. A solution of  $H_2S$  in benzene may be used after gas treatment with  $SO_2$ . (18) Vulc. of gutta percha and balata with  $H_2S$  and  $SO_2$ . (19) Vulc. of thin layers of R. or R. cement by gases. Addition of the two gases to separate cements, mixing the cements, and evaporating the solution whereby a layer of vulc. R. is produced. (20) Use of  $H_2S$  and  $SO_2$  under pressure. (22) Lecture on Peachey process with description of factory methods. (23) Spreading of vulcanized gels on fabric. (25) Use of  $SO_2$  in the gas vulc. of R. (26) See Benzoquinone.
- Peachey, S. J. & Skipsey, A. (1) Use of lake pigments in R. goods cured by Peachey process. (2) See Ultramarine blue. (3) Vulc. of gutta percha or balata in sheet or solution by treatment with  $H_2S$  and  $SO_2$  at ordinary temp.
- Pierron, L. (1) Peachey process.
- Skellon, H. (4) Pentathionic acid believed to function in the Peachey process.
- Stevens, H. P. (28) Peachey process. (33) Moisture does not interfere with the Peachey process and possibility of porosity is thereby reduced to a minimum. (35) Peachey Process. (69) Peachey's process applied to latex precipitates S without vulc.
- Venable, C. S. & Fuwa, T. (1) Solubility of  $H_2S$  and  $SO_2$  in R.
- Wilhelm, G. (2) Peachey Process.
- Pentamethylenediamine.**  
**Cadaverine.**  
 1, 5-Diamino Pentane.  
 Bayer & Co. (13) Use in synth. R. (14) A powerful accel.  
 Bruni, G. (1) Mentions the dithiocarbamates of this base. See Dithiocarbamates.
- Pentamethylenetetramine.**  
 Dubosc, A. (30) An accel.
- Pentamethylenethiuramdisulfide.**  
 Romani, E. (1) A vulc. agent and an accel.
- Pentamethyl-pararosaniline.** See Methyl Violet.
- Pentoxyphenyl-pentoxo-rubber.**  
 Ditmar, R. (47) p. 42.  
 Gottlob, K. O. (7) p. 5.  
 Weber, C. O. (14) By reaction of phenol and R. tetrabromide.
- Peptones.** See Protein.  
 Dubosc, A. (23) Mentioned.  
 Eaton, B. J. & Grantham, J. (4) Weak accels.  
 Eaton, B. J., Grantham, J. & Day, F. W. F. (1) Casein and peptone have no effect on rate of cure when added to a R. mix but when decomposed they act as accels.  
 Fickendey, E. (2) In Funtumia latex a peptone and not a protein acts as the protective colloid.  
 Skellon, H. (1) Peptone influences the cure more than casein.  
 Stevens, H. P. (2) Peptone and, to a smaller degree, casein perform the same function as the insoluble matter of R.
- Perbenzoic Acid.**  
 Ostromuiskenskii, I. (11) (25) (30) Used for the vulc. of R. by oxygen

- Pummerer, R. (1) R. in  $\text{CHCl}_3$  at  $0^\circ\text{C}$ . gels in 45 min. with perbenzoic acid.
- Pummerer, R. & Burkard, P. A. (1) Oxidizes R. in  $\text{CHCl}_3$  solution giving a compound of the composition  $(\text{C}_6\text{H}_5\text{O})_x$ .
- Stevens, H. P. (10) Perbenzoic acid can replace benzoyl peroxide as a vulcanizing agent.
- Perborates.**
- Persulfates.**
- Perchlorates.**
- Bernstein, G. (6) Prevention of black color in litharge mixings.
- Permanganates.** See Potassium Permanganate.
- Harries, C. (31) p. 50. Action on R.
- Pummerer, R. (1) Action on R.
- Permeability of Rubber.** See Gases.
- Peroxidase.** See Enzymes.
- Peroxides.** See Acetone Peroxide, Benzoyl Peroxide, Ozone and Perbenzoic acid.
- Ostromuiskenskii, I. (11) Metallic oxides are inactive in vulc. of R. by peroxides and increase tendency to oxidation. Colophony and resins diminish value of vulc. product. A mixture of metallic oxides and amines retard vulc. by this method. Proteins have the same effect as with S the strength of the product is increased.
- Persulfates.**
- Dubosc, A. (30) (40) See Sulfur Dioxide.
- Phenanthrene.**
- Phillips, R. O. (1) Use in R.
- Phenetidine.** See p-Aminophenetol.
- Phenol.**
- Carbolic Acid.**
- Anon. (99) See Latex-Preservatives.
- Brindejone, G. (1) See Light.
- Davidson, S. C. (1) (2) (3) (4) (5) (6) See Latex-Preservatives.
- Dubosc, A. (15) See Ageing-Oxidation. (30) (40) See Sulfur Dioxide. (49) Action of phenols on regenerated R.
- Eaton, B. J. & Whitby, G. S. (1) Phenol and cresol added to latex retard the rate of cure of smoked sheet and cause rapid oxidation and darkening.
- Kratz, G. D., Flower, A. H. & Coolidge, C. (1) Phenol retards vulc. See Aniline.
- Maximoff, A. (1) Phenol with  $\text{PbO}$  aids the curing action of thiuram disulfides.
- Moureaux, C. & Dufraisse, C. (1) See Ageing-Oxidation.
- Porritt, B. D. (4) Phenol and cresol used as solvent for caustic for use as an accel.
- Scholz, V. (1) See purification of R.
- Stevens, H. P. (71) See Latex-Preservatives.
- Twiss, D. F. (6) Sodium phenolate as an accel.
- deVries, O. (24) p. 92. Phenol and sulfuric acid used to coagulate latex. Rate of cure is decreased.
- Whitby, G. S. (4) See Ageing-Oxidation.
- Phenol-formaldehyde condensation products.**
- Speedy, A. & Crouch, A. P. (1) Used as compounding ingredients in R.
- Phenyl-dithiocarbamic acid.** See Dithiocarbamates.
- p-Phenylene Diamine.**
- Anon. (84).
- Bayer & Co. (19) R-100, S-10, Accel.-2. Cure 15 min./3 atm.
- Bedford, C. W. & Sebrell, L. B. (1) Reacts with S during vulc. to form ammonium polysulfide. Will not air cure a  $\text{CS}_2$  cement containing  $\text{ZnO}$ .
- Boggs, C. R. (3).
- Ditmar, R. (62) A rapid accel.
- Dubosc, A. (30) (42) (40) All para diamines react with S at  $140^\circ\text{C}$ . to give  $\text{H}_2\text{S}$ .
- Earle, D. (1) Most poisonous of all the accels. now in use. Inhalation of dust is chief danger.
- Endres, H. A. (1) Comparison of several accels.
- Gottlob, K. O. (7) (9) A strong accel
- Hasselt, J. F. B. van. (1) See p-Nitrosodimethylaniline.
- King, A. H. (1).
- Kratz, G. D., Flower, A. H. & Coolidge, C. (1) Aromatic diamines are more

- powerful than mono amines if the groups are in the para position. This accel. is almost twice as active as Aniline. See Aniline.
- Kratz, G. D., Flower, A. H. & Shapiro, B. J. (1) See Aniline.
- Kryder, F. L. (1) Used in reclaiming.
- Meeus, E. de. (1) R-90, S-3, Accel.-5. Cure 1 hr./135° C.
- Meissner, R. (1) Effect of this diamine on frogs and rabbits described.
- Murrill, P. I. (5).
- Pearson, H. C. (1) p. 84. Data from the Bayer Co.
- Pickles, S. S. (1).
- Rosenbaum, J. L. (1).
- Scott, W. & Bedford, C. W. (1) Reacts with S at curing temp. to produce H<sub>2</sub>S and NH<sub>3</sub> which with free S forms ammonium polysulfide.
- Twiss, D. F. (12).
- Twiss, D. F. & Brazier, S. A. (1) See Phenylene diamines.
- Weber, L. E. (9) Has no place in the R. industry due to its frightfully poisonous properties.
- Phenylene Diamines.**
- Bayer & Co. (19) mentioned as accels.
- Boggs, C. R. (3) See p-Phenylene Diamine.
- Cadwell, S. M. (3) See Aldehyde-Amines.
- Ditmar, R. (24).
- Dubosc, A. (60) See Dyes.
- Eaton, B. J. (8).
- Gottlob, K. O. (7) (9) The meta and ortho isomers are inactive as accels. (8) Used in synth. R.
- Kratz, G. D., Flower, A. H. & Shapiro, B. J. (1) See Aniline.
- Meeus, E. de. (1) Mentions m-phenylene diamine as an accel.
- Ricard, E. (2).
- Twiss, D. F. & Brazier, S. A. (1) The meta isomer is less active than the para. Data and curves.
- Phenylethylamine.**
- Ostromuiskii, I. (13) (25) An accel.
- Phenylguanidine.** See Monophenylguanidine.
- Phenylhydrazine.** See Aldehyde-Amines.
- Anon. (255).
- Bayles, E. A. (1) A retarder of vulc. of R. See Dinitrosophenol.
- King, A. H. (5).
- Kratz, G. D., Flower, A. H. & Shapiro, B. J. (1) See Aniline.
- Naylor, R. B. (2) Patented as an accel.
- Peachey, S. J. (11) A negative accel. even in small amounts.
- Phenyliminomethane.** See Methyline Aniline.
- Phenylisothiocyanate.** See Phenyl Mustard Oil.
- Phenyl Mustard Oil.**
- Bruni, G. (1) See Sulfur Reaction Products.
- Bruni, G. & Romani, E. (1).
- Earle, D. (1) Formed by heating thiocurbanilide to vulcanizing temp. See Poisoning.
- Twiss, D. F. (12) A weak accel. in presence of ZnO.
- Phenylthiourea (mono.).**
- Bruni, G. (1) Reacts with S to form mercaptobenzotriazole.
- Kratz, G. D., Flower, A. H. & Coolidge, C. (1) Less active, weight for weight, than thiocurbanilide. See Aniline.
- Phosphoric Acid.**
- Gibson, W. T. (1) A coagulant for Kickxia latex.
- Phosphorus.**
- Anon. (270) Phosphorous has been combined with R. to produce an effect similar to that of S.
- Kaye, F. (3) Phosphorous content of hevea latex is variable.
- Phosphorous thiobromide.**
- Phosphorous thiodide.** See Mercury Halides.
- LeRoy, G. A. (1) Vulc. of R. cements by thiodides or thiobromides of phosphorous, arsenic, nitrogen or antimony. The process is accelerated by aromatic nitro compounds such as nitrophenol, nitrotoluol, nitronaphthol, trinitrophenol, etc. or by metals such as Hg, Sn, Pb or Ag. The metallic iodides or bromides may also be used with free S. The sulfides of phosphorous, arsenic or antimony may be used with bromine or iodine.

**Phosphotungstic Acid.**

Eaton, B. J. (23) & (25) Retards rate of cure when used to coagulate latex and also when mixed into dry R. prior to vulc. See Tannin.

Whitby, G. S. (5) Produces a flocculent precipitate but not a coherent clot when added to latex.

**Phytosterol.**

Cohen, N. H. (2) Phytosterol ( $C_{27}H_{46}O.H_2O$ ) is present in alcohol soluble resin of Euphorbia R. This is identical with ischolesterol from wool fat.

Dietrich, K. (2) Phytosterols in wild R.

Dubosc, A. (14) Phytosterol from Jelutong resins.

Hillen, G. H. (1) Guayule R. contains no phytosterols.

**Picramic Acid.**

Ostromuiskenskii, I. (22) See Colophony. (25) See Dinitrobenzene.

**Picric Acid.**

Alexander, P. (4) An additive product of R. with picric acid can be made.

Ostromuiskenskii, I. (22) See Colophony. (25) See Dinitrobenzene.

**Picryl Chloride.**

Ostromuiskenskii, I. (22) See Colophony. (25) See Dinitrobenzene.

**Piperidine.**

Anon. (84).

Badische Co. (6) MgO and piperidine are used in synth. R.

Bayer & Co. (5) Piperidine or homologues as accels. R-100, S-10, Accel.-0.5. Cure 15 Min./135°-145° C. Sc = 3.5%. R-100, S-40, Accel.-0.75. Cures to ebonite 2 hrs./155° C. Sc = 25%.

(6) Derivatives of piperidine and its homologues as accels.

(7) Used in synth. R. (8) Synth. R-100, S-10, Accel.-0.75. Cure 1 hr./120°-125° C. or 15 min./135°-145° C.

(9) Piperidine derivatives, n-thiopiperidine and benzal dipiperyl as accels. for synth. R. (13) Used in synth. R. Formulæ given. (14).

(28) Used to improve the ageing of balloon fabric. See Ageing.

Blanc, M. le & Kröger, M. (1) See Viscosity.

Dannerth, F. (1).

Ditmar, R. (62).

Dubosc, A. (40) Piperidine is mixed with S. before compounding. It reacts with S. during the cure. (52) Piperidine used in Akron in 1909.

Duisberg, C. (1) Piperidine added to synth. R. prevents oxidation and facilitates vulc. yielding a hard rubber. (2) Piperidine, etc., added to synth. R. as accel. gives a hard rubber comparable to that from natural R.

Eaton, B. J. (4). (8).

Geer, W. C. (2).

Gottlob, K. O. (7). (8). (9) See Piperidine-pentamethylene Dithiocarbamate.

King, A. H. (1).

Maximoff, A. (1).

Murrill, P. I. (5).

Ostromuiskenskii, I. (17) Piperidine heated with PbO and S forms a viscous mass which is believed to be identical with the S<sub>2</sub> obtained by Erdman. (21) Piperidine accelerates the vulc. of R. without sulfur by nitro compounds. (25) Used to prevent ageing in R. cured without S. See Dinitrobenzene.

Pearson, H. C. (1) p. 85.

Ricard, E. (2).

Rosenbaum, J. L. (1) ZnO increases its curing power.

Rossem, A. van. (6) Comparison with aldehyde ammonia and accelerene by means of coefficient of vulc.

Schidrowitz, P. (43) An accel. is prepared by synthesizing a carbon disulfide derivative of an organic base, such as CS<sub>2</sub> on piperidine, on a carrier such as Clay. A good mix will age far better than a parallel unaccelerated mixing. (52) See Latex-Vulcanization.

Simmons, H. E. (1).

Spence, D. (21) & (26) R-100, S-10, Piperidine-1. The results of this test were published six months before the Bayer Co. patent was applied for. (27) Used for devulcanization of R. (28) Claims discovery of piperidine through compounds published in D. Spence (10) in which he states were cured with this accel.

Twiss, D. F. & Brazier, S. A. (1).

**Piperidine-pentamethylene Dithiocarbamate. (Vulcacite P.)**

- Anon. (48) (286) See Suparac Accels.  
 Badische Co. (6).  
 Bayer & Co. (5) Homologues of piperidine as accels. (6) Derivatives of piperidine as accels. (29) Method of preparation. (37) Used as an accel. in the preparation of factis.  
 Bean, P. L. (2) PbO prevents air curing of a R-S-ZnO mix containing this accel., retards the first part of the cure but gives the same ultimate effect as ZnO.  
 Bedford, C. W. & Scott, W. (1).  
 Bruni, G. (1) See Dithiocarbamates.  
 Bruni, G. & Romani, E. (1).  
 Maximoff, A. (1) A strong accel.  
 Murrill, P. I. (5) A very powerful accel.  
 Ostromuiskenskii, I. (5) Used with MgO at 284° F. (13) Use with PbO and MgO. Piperidine compounds need metallic oxides to bring out their full curing power. (14) Mentioned for curing Peruvian R. Works exceptionally well in synth. R. (16) Use with MgO. (21) Prevents ageing of R. cured with nitro compounds and PbO. (22) Used with ZnO and MgO in synth. R. (31) R-100, S-5, PbO-10, Accel.-1. Mix on hot rolls. Will complete its cure at room temp. in 3 days. R-100, Dye-30, ZnO-20, S-8, Accel.-2. Cure 10 Min./140° C. or 15 hrs./50° C. or stand 3 days and cure 2 Min./140° C. Dyes which lose their color at 150° C. may be used at 50° C.  
 Ostromuiskenskii, I. & Kelbasinskaya, I. M. (1) Used in manufacture of synth. R.  
 Rosenbaum, J. L. (1) Easily decomposed.  
 Schidrowitz, P. (43) This accel. is made in contact with and dispersed on clay, chalk or magnesium carbonate.  
 Schidrowitz, P. & Bean, P. L. (1) Effect of this accel. with varying concentrations of S. For 0.5% Accel. between 2 to 2½% S. is best.  
 Schidrowitz, P. & Burand, J. R. (1) Effect of this accel. on R. stress-strain curve. ZnO is necessary. Coefficients, curing curves and ageing data. Better ageing is due to low

vulc. temp. and because the accel. is destroyed or rendered inactive by secondary reactions during or after vulc.

- Scott, W. & Bedford, C. W. (1) Will get a R-S-ZnO cement at ordinary temp. in 24 hrs. while piperidyl ammonium polysulfide has no effect.  
 Twiss, D. F. (12) Graphs for R-90, S-10, Accel.-0.25 with and without ZnO. (14).  
 Twiss, D. F., Brazier, S. A. & Thomas, F. (1) Variation of time, temp. ZnO and Accel. Graphs, coefficients and testing data.  
 Whitby, G. S. & Smith, A. H. (1) The speed of vulc. with this accel. is greatly increased in the presence of ZnO.  
 Whitby, G. S. & Walker, O. J. (1) Comparison with Hexa, thiocarbamilide, etc. Tests and ageing data. (2) Effect of piperidinepentamethylene-dithiocarbamate on coefficient of vulc., time of cure, tensile strength, elongation, etc.

**Piperidylurea.**

- Bayer & Co. (5) R-100, S-50, Accel.-1. Cure 45 Min./155° C. to ebonite. With S-10, cure at 125° C. to soft R. (6) Mentioned.

**Pitches.**

- Dannerth, F. (4) Effect on Ageing. See Ageing.

**Platinum.**

- Thomson, W. & Lewis, F. (1) See Copper.

**Poisoning by ingredients used in Rubber.**

- Albaugh, R. P. (1) Effect of benzol on workmen and treatment of cases of benzol poisoning.  
 Anon. (43) Cases of chronic benzol poisoning in the R. industry. (45) Lead poisoning. (51) Poisoning by CS<sub>2</sub>. (53) Court record on a case of poisoning by CS<sub>2</sub>. (95) Aniline poisoning. (98) Benzol poisoning. (128) Accelerene and thiocarbamilide are poisonous. K glyceride is harmless. (139) Dangerous procedures in the R. industry. (147) Poisoning by CS<sub>2</sub> (1887). (149) Poisonous pigments used in R. Sb and Cd sulfides



- or water insoluble zinc compounds are not poisonous. (212) Discussion of the use of  $\text{CS}_2$ ,  $\text{S}_2\text{Cl}_2$  and  $\text{C}_6\text{H}_6$ . (218) Handling  $\text{PbO}$  in R. factories. (294) Poisons used in the R. industry. Lead Compounds. Crimson antimony is three times as poisonous as Golden antimony. Aniline destroys the red corpuscles. Benzol causes respiratory paralysis, especially in females. Solvents. Reduction of hazards. (302) Lead poisoning.
- Birchall, F. W. (1) Poisoning by  $\text{S}_2\text{Cl}_2$ .
- Bulowsky, A. (1) Poisonous character of certain R. articles.
- Camille, A. (12) Naphtha fumes overcome workmen, producing an effect similar to laughing gas. (17) While medical experts hold that exposure to naphtha fumes does not produce any definite disease, it is shown that inhalation of the vapors is incompatible with life.
- Dannert, F. (1) Discussion.
- Davenport, B. F. (1) Poisonous colors in R. goods.
- Davis, P. A. (1) See Aniline.
- Delpech. (1) Diseases of R. workers. (2) Accidents to R. workers. Inhalation of  $\text{CS}_2$ .
- Ditmar, R. (18) Antimony sulfide in R. goods is non-poisonous.
- Earle, D. (1) Report of committee on the poisonous nature of accels. Aniline and similar poisoning.
- Esch, W. (17) Red nipples containing antimony sulfides are not injurious.
- Gaisman, L. (1) p-nitrosodimethylaniline is not poisonous.
- Gottlob, K. O. (6) Vermillion is non-poisonous.
- Hamilton, A. & Luce. (1) Aniline poisoning. (2) U. S. Bureau of Labor Statistics report.
- Horan, C. F. (1) Lead and accelerator poisoning. (2) Practically impossible for a workman to contract lead poisoning unless exposed to mixing hazard. Poisoning at the mixing mill depends on the individual. (3) Benzol poisoning.
- Klein, C. A. (1) Hygiene in the R. industry. Volatile solvents. Lead compounds.
- Kratz, G. D. (2) Ichthyol recommended as a treatment for Hexa rash.
- Kulka, W. & Humma, E. (1) Effect of hydrogen sulfide in the air.
- Landerheimer, R. (1) Traces of  $\text{H}_2\text{S}$  found in all  $\text{CS}_2$ . Thorough study of  $\text{CS}_2$  poisoning.
- Lascelles-Scott, W. (6) Toxicity of  $\text{CS}_2$ .
- Legge, T. M. (1) Description of three fatal cases of benzene poisoning of victims who were constantly working with R. solutions.
- Luff, B. D. W. (2) Regulations for use of lead.
- Lutz, L. (1) Poisons in R. nipples. Antimony.
- Meissner, R. (1) See p-phenylenediamine.
- Meyer, L. O. P. (1) The use of lead in any form, copper or uranium is forbidden in non-poisonous articles in Germany (1892). Cinnabar is non-poisonous.
- Murril, P. I. (5) p-Phenylenediamine is very toxic.
- Oliver, T. (1) Lead accumulates in the body. (2) Women are more susceptible to lead poisoning than men. Treatment for lead poisoning.
- Peachey, S. J. (24) Thiocarbamide, formaldehyde-aniline and aldehyde-ammonia cannot be taken internally without bad effects. There is little to choose between toxicity of formaldehyde-aniline and p-nitrosodimethylaniline. p-Nitrosodimethylaniline causes dermatitis on certain people.
- Pearson, H. C. (1) p. 82. Prevention of aniline poisoning. p. 103. Lead poisoning.
- Phelps, E. B. & Stevenson, A. F. (1) Use of antimony in articles for infants is undesirable.
- Pugliese, A. (1) Toxic action of benzene (benzol). (2) Toxic action of benzene (petroleum ether) and toluene.
- Quinby, R. S. (1) Medical supervision in R. plants.
- Rosenbaum, J. L. (1) Discussion.
- Sabbatani, L. (1) Antidotes for hydrogen sulfide poisoning.
- Sanders, W. W. (1) Aniline poisoning.
- Schidrowitz, P. (39) Aniline poisoning. (49) Poisoning by lead compounds. Prevention.
- Shephard, N. A. & Krall, S. (1) Poisoning by Hexa is confined to han-

- dling of uncured stocks. The rash is in greatest evidence during warm weather when workmen perspire freely. It is prevented by washing with a saturated solution of  $\text{NaHCO}_3$ .
- Springer. (1) Poisoning by  $\text{S}_2\text{Cl}_2$  and  $\text{CS}_2$ .
- Terry, H. L. (3)  $\text{S}_2\text{Cl}_2$  although disagreeable has not been found to undermine the health of workmen. Carbon disulfide is detrimental to health.
- Uchinsky. (1) Poisoning by hydrogen sulfide.
- Utz, K. (1) Lead poisoning by R. cloth.
- Weber, C. O. (22) Sanitation in use of lead compounds is emphasized.
- Weber, L. E. (9) Lecture on poisoning by aniline, hexa, methyleneaniline, etc.
- Polymerization.** See Depolymerization.
- Axelrod, S. (1) See Vulcanization-Theories.
- Boggs, C. R. (3) See Vulcanization-Theories.
- Gottlob, K. O. (11) p. 89. part 2. Résumé of literature.
- Gottlob, K. O. & Miksch, K. (1) R. polymerizes during drying.
- Polysulfides.**
- See Ammonium Sulfide, Polysulfide, Potassium Polysulfide, Sodium Polysulfide, Calcium Pentasulfide.
- Bedford, C. W. & Sebrell, L. B. (1) See m-Toluylenediamine.
- Bolas, T. (3) Extra S is necessary with  $\text{Sb}_2\text{S}_3$ ,  $\text{PbS}$ ,  $\text{HgS}$  or  $\text{ZnS}$ . The sulfides have very little vulcanizing action. Alkali or alkaline earth polysulfides will vulcanize R.
- Bourquin, H. (1) Mentions hydrogen, sodium and calcium polysulfides.
- Bruni, G. & Amadori, M. (1) Solutions of S in  $\text{S}_2\text{Cl}_2$ .
- Davidson, S. C. (3) (4). See Latex-Coagulation.
- Esch, W. (6)  $\text{MgS}_x$  is a powerful sulfur carrier.  $\text{ZnO}$  does not form polysulfides.
- Gmelin, L. (1) p. 349. Gerard vulc. R. with  $\text{K}_2\text{S}_8$  at  $140^\circ \text{C}$ .
- Marckwald, E. & Frank, F. (11) Metallic sulfides and polysulfides as acceler.
- Marzahn, R. (1) p. 467. Polysulfides assist vulc.
- Mayer, A. M. (1) A thin layer of ebonite held to the sunlight looks red.
- Mourey, (1) Vulc. of R. in a 12% ammoniacal solution of R.
- Porritt, B. D. (2).
- Richards, Taylor & Wylde. (1) See Alkali.
- Schidrowitz, P. (52) See Latex-Vulcanization.
- Spence, J. B. (1) Metallic sulfides of Ca or Fe are heated with molten S cooled and ground. The powder is used as a vulcanizing agent for R.
- Pontianac Rubber.**
- Alexander, P. (2) See Oxygen compounds in Rubber.
- Weber, C. O. (21) The acetone insoluble portion resembles low grade R. and gives a  $\text{C}_{10}\text{H}_{16}\text{Br}_4$  product. India R. portion— $\text{C}_{40}\text{H}_{60}\text{O}_{10}$ ; Insoluble resin— $\text{C}_{40}\text{H}_{60}\text{O}_8$ ; Soluble resin— $\text{C}_{40}\text{H}_{60}\text{O}_8$ .
- Porosity.**
- Anon. (53) Prevention of. See Manganese Sulfide. (131) M. Payen states that R. is porous during vulc. 0.3% water is sufficient to render stock porous. (235) Caused by moisture in the various compounding ingredients. (254).
- Heschus, N. (1) Contraction of stretched R. is not due to porosity.
- Höhn, J. B. (2) Porosity may be due to moisture, to action of condensing steam or formation of some gaseous compound in R.
- Hübener, G. (10) Interior porosity is due to poorly conducted vulc.
- Iterson, G. van. (1) (2) Porosity is due to moisture. Undervulcanized R. is plastic and has weak resistance to tension produced by water vapor. A porous product can be obtained with any mix by undercuring in steam and then quickly blowing off the steam.
- Minder, J. (5) Causes of porosity and how it may be avoided.
- Pellier, P. (1) The action of S on oxidized R. can form  $\text{H}_2\text{SO}_4$  which forms bubbles. Quick lime prevents porosity.
- Roux, le. (1) Porosity of R.
- Schulze, E. (8) Porosity is due to the method used for vulcanizing. Poros-

ity is caused by the fact that at certain temperatures the R. is so soft that it has no resistance to the pressure of the gases in the mixture.

Weber, C. O. (24) Due to moisture and  $H_2S$  which is generated by the action of S. on the resins and oils.

#### **Potassium.**

Gottlob, K. O. (7) p. 71. K, Na or Li are unuseful in R. since they change it to a porous mass during vulc. which easily absorbs moisture.

Twiss, D. F. (6) Potassium with aniline, diphenylamine and toluidine as accel. of vulc.

#### **Potassium Bisulfate.**

Rossem, A. van. (6)  $KHSO_4$  retards vulc.

#### **Potassium Carbonate.**

Eaton, B. J. (16) Added to coagulating bath, it accelerates the vulc. of the resulting R.

#### **Potassium Glyceride.**

Anon. (128) A non-toxic accel. whereas accelerene and thiocarbanilide are toxic.

#### **Potassium Hydroxide.** See Sodium Hydroxide.

Beadle, C. & Stevens, H. P. (16) R. treated with a solution of alkali perishes rapidly.

Ditmar. (62) W. G. Martin says that 3% of NaOH, KOH and  $Ca(OH)_2$  acts as an accel.

Eaton, B. J. (9) R. soaked in solution of NaOH or KOH shows increased rate of cure. R. becomes tacky on ageing.

McCurdy, D. (1) Added potash and S to R. prior to vulc. (1851).

Obach, E. F. A. (1) KOH, sp. gr. 1.28, has no appreciable action on gutta percha.

Stevens, H. P. (15) G. Bernstein mentions the use of potash in glycerin prior to D. F. Twiss.

Twiss, D. F. (4) W. G. Martin showed that a small amount of KOH powder added to R. and S increases the degree of vulc.

Twiss, D. F. & Brazier, S. A. (1).

#### **Potassium Oxalate.**

Anon. (99) See Latex-Preservatives.

#### **Potassium Permanganate.**

Arens, P. (6) Effect on R.

Boswell, M. C. (1) See Oxidation.

Harries, C. (6)  $KMnO_4$  added to benzol solution of R. On evaporation a syrup was obtained but an analysis showed that only depolymerization had taken place. (31) p. 50.

Morgan, S. (1) See Enzymes.

Ostromuiskii, I. (11) (19) Vulc. of R. by.

Raymond, J. M. (1) See Ageing-Tackiness.

#### **Potassium Stearate.**

Price, R. B. (1) See Thiocarbanilide.

#### **Potassium Sulfides.** See Sodium Sulfides

Anon. (158)  $K_2S_8$  as a vulcanizing agent. (160) See Vulcanization.

Gerard, A. (1) A 25° Baume solution of  $K_2S_8$  is brought to boiling. R. articles are vulcanized by dipping in the hot solution.

Gmelin. (1) p. 349. A. Gerard's process.

Hancock, Chas. (4) Alkaline sulfides used in preparation of gutta percha.

Heinzerling, C. (1) p. 48.  $K_2S_8$  in an aqueous solution as a vulcanizing agent for R.  $K_2S_8$  and  $K_2S_6$  act like  $K_2S_8$ . p. 65. Potassium trisulfide or pentasulfide mixed with  $ZnO$ ,  $ZnCO_3$  or lime. .8% to 12% of this mixture is added to R. and a good vulcanized product is obtained.

Koller, P. (1) Use of  $K_2S$  to prevent tackiness.

Moulton, S. (2) Use of alkaline sulfides to vulcanize R.

Pearson, H. C. (1) p. 68. A. Gerard's process.

Pickles, S. S. (1)  $K_2S_8$  will vulcanize R. without free S.

Twiss, D. F. (12) An accel. composed of KOH in glycerine (1:3) saturated with  $H_2S$ .

#### **Potassium Xanthates.** See Xanthates.

#### **Propionaldehyde.**

Cadwell, S. M. (3) See Aldehyde-Amines.

#### **Propionaldehyde-aniline.**

#### **Propionaldehyde-mono-ethylamine.**

Cadwell, S. M. (3) See Aldehyde-Amines.

**Propyl Alcohol.**

Ostromuiskii, I. (13) Propyl alcohol with metallic oxides as an accel. of vulc.

**Propyl Dithiocarbamates.** See Dithiocarbamates.

Molony, S. B. & Nikaido, Y. (1) Accelerators.

**Propylene diamine.**

Ostromuiskii, I. (25) (13) An accel.

**Protein.** See Albumin, Casein, Natural Accelerators, Peptones.

Anon. (84). (122) R. proteins accelerate vulc. (125) Albumin is an accel. of vulc. (250) Proteins tend to lump on the mixing rolls. This is overcome by using their Ca or Mg salts.

Barritt, N. W. (1) Glue can replace the insoluble matter in R. and perform the same function during vulc.

Beadle, C. & Stevens, H. P. (5) Protein content of latex. (8) R. proteins belong to a group of the mussines i.e. a glycoprotein. This on heating in a sealed tube at 130° C. gives HCNS, H<sub>2</sub>S and glucose. R. proteins only gave HCNS and H<sub>2</sub>S. (10) Effect of natural proteins on the vulc. of R. (12) Insoluble constituents of Ceara Rambong R. act as S carriers but independent of the amount of N present. (13) Insoluble matter of R. plays an important rôle in vulc. See Latex.

Bedford, C. W. (1) Sulfur reaction products of proteins mentioned as accels. of vulc. (3) Hydrolyzed proteins and their carbamates as accels. of vulc. (5) Reclaiming of vulc. R. which contains added protein.

Bernstein, G. (4) R. solution exposed to ultra violet light with exclusion of air results in depolymerization of the R. The insoluble matter of the R. can be filtered off.

Blossom, T. M. (1).

Budde, T. (B) Effect of protein in tetrabromide analysis.

Caspari, W. A. (5) Separation of insoluble constituents of R.

Dubosc, A. (7) & (26) See Vulcanization-Theories. (8) Determination

and identification of proteins in R. (30).

Eaton, B. J. (4) The mixture of egg albumen and lime used by W. Esch (1) produces hydrolyzed proteins similar to the biological degradation products of natural R. proteins.

Eaton, B. J. & Grantham, J. (2) Proteins act as catalysts during vulc. (4) Decomposed proteins are responsible for the curing power of Plantation R. (5) See Variability.

Esch, W. (13) Addition of protein to R. with lime or MgO and insolubilizing the protein with smoke or tannin. Egg albumin is used.

Faraday. (1) Established presence of proteins in R. in 1826.

Fendler, G. (5) Effect of insoluble matter of R. on the bromination of R.

Fendler, G. & Kuhn, O. (1) The insoluble part of R. is not insoluble, it is only difficultly soluble.

Pickendey, E. (2) Proteins and peptones as protective colloids.

Flamant, G. (1) Proteins in Congo R. See Colloid Chemistry, and Latex.

Frank, F. (9) Coagulation of latex should be carried out in such a way that the albumins remaining in the R. are present in a form that is not liable to disintegration. Phenylalanine, tyrosin, tryptophane, some diamino acids and with fair certainty a mono amino dicarboxylic acid and cystine were isolated in proteins of R. and latex.

Frank, F., Gnaedinger, J. & Marckwald, E. (1) Optically active proteins in Kickxia latex.

Frank, F. & Marckwald, E. (5) Nitrogenous substance in raw R. and in latex is a true protein, yielding amino acids on hydrolysis.

Green, J. R. (1) Manihot glaziovii R. contains a peptone-like body and a globulin. HNO<sub>3</sub> on the aqueous portion of the latex, precipitates a white amorphous substance identical with Faraday's albumin.

Heinemann, A. (1) Proteins or proteids impart to synth. R. the nerve and elasticity of natural R.

Heurn, F. C. van. (7) R. serums are hygroscopic and if not thoroughly

- washed out cause "white stripe" in the center of the sheet.
- Johnson, W. (1) Use of gluten, flour, resins, etc., in R.
- Jong, A. W. K. de & Tromp de Haas, W. R. (1) Castilloa latex coagulated with alcohol contained no nitrogen and therefore no protein.
- Kaye, F. (1) Oxidation of proteins causes coloration of R.
- Kempel, A. D. (1) Glue is an accel.
- King, A. H. (1).
- Lamberthy, E. (1) The protein content of R. is increased by the use of egg albumen.
- Lascelles-Scott, W. (1) See Latex.
- Marzahn, R. (1) p. 144.
- Ostromuiskii, I. (13) Egg albumen, peptone, gum arabic and gelatine are without effect on the tensile strength of synth. R.
- Rosenbaum, J. L. (1).
- Rossem, A. van. (4) Nitrogen and proteins in raw R.
- Rossem, A. van & Dekker, P. (1) Nitrogen is not all present in R. as protein. R. heated  $\frac{1}{2}$  to 3 hrs./110°-130° C. in CO<sub>2</sub> increases the insoluble part of the R.
- Schmitz, W. C. (3) Proteins of plantation and Para R. The quality of R. is more dependent on the resins than on the proteins.
- Schon & Son. (1) See Purification of Rubber.
- Semler, H. (1) Proteins in R. latex.
- Spence, D. (2) The protein is distributed in fiber-like threads throughout the R. (15) The insoluble constituent of R. is the protein. Proteins and S give H<sub>2</sub>S in hot vulc. The proteins may be the cause of "blowing" in certain cases. Thorough washing and drying prevents decomposition of the protein. Para R. contains a peroxidase enzyme. Proteins resemble gluco proteins or mucins. (15) See Enzymes. (17) See Bromine. (21) The insoluble constituent of R. is a nitrogen containing protein.
- Spence, D. & Kratz, G. D. (1) The protein of plantation R. possesses the characteristics of a gluco-protein.
- Stevens, H. P. (1) Separation of R. proteins by solvents. (2) Peptones and casein will replace the natural proteins in R. (73) Influence of proteins on colloid behavior of R.
- Thal, J. R. (1) Chemical investigation on R. proteins.
- Tschirch, A. & Schmitz, W. (1) Separation of proteins from R.
- Vernet, G. (3) Coagulation of latex is due to protein precipitation. See Latex-Coagulation.
- deVries, O. (26) Dilution of latex with serum has no effect on the keeping qualities of the R. A more rapid vulcanizing R. results.
- Weber, C. O. (36) Castilloa R. freed from proteins remained white in air and light. Darkening of R. is due to presence of proteins.
- Whitby, G. S. (8) p. 108. Extensive résumé of literature on R. proteins.
- Purub.** See Hydrofluoric Acid and Latex-Coagulants.
- Putrescence.** See Tetramethylenediamine.
- Pyroligneous Acid.** See Latex-Coagulants-Acetic Acid.
- Pyridine.**
- Bayer & Co. (5) (13) Not an accel.
- Gottlob, K. O. (7).
- Kratz, G. D., Flower, A. H. & Coolidge C. (1) Reference to Wo. and Wa. Ostwald.
- Ostromuiskii, I. (21) Used to prevent ageing in R. cured with nitro compounds. It also accelerates the cure. (25) See m-Dinitrobenzene.
- Ostwald, Wa. (1) See Ageing-Tackiness.
- Ostwald, Wo. & Ostwald, Wa. (1) Prevents the ageing or hardening of R.
- Stevens, H. P. (71) See Latex-Preservatives.
- Pyrogallol.**
- Bayer & Co. (41) See Ageing-Tackiness.
- Heilbronner, A. (1) See Tannin.
- Moore, L. R. (1) Used in R. cements to prevent oxidation.
- Whitby, G. S. (4) Pyrogallol added to latex before coagulation does not affect the R. from standpoint of vulc.
- Pyromucic Aldehyde.** See Furfural.

**Pyromucic Aldehydeammonia.**

Ricard, E. (1) An accel.

**Pyrrolidine.****Tetrahydropyrrrol.**

Bayer & Co. (13) The reaction product of pyrrolidine and CS<sub>2</sub> as an accel. for the vulc. of ebonite.

Ditmar, R. (62).

King, A. H. (1).

Murrill, P. I. (5) A very powerful accel.

Whitby, G. S. (8) p. 190. An accel. Pyrrole derivatives have been found in matured R.

**Pyrrolidine Dimethylamine.**

Bayer & Co. (6) Mentioned as an accel.

**Quaternary ammonium bases.**

Bayer & Co. (19) Mentioned as accels.

Ditmar, R. (62) Give rapid acceleration of vulc.

Dubosc, A. (40).

Eaton, B. J. (8).

King, A. H. (1).

**Quebrachite.** See 1-Methyl Inositol.

Beadle, C. & Stevens, H. P. (13) 0.8 to 1.6% of quebrachite in the dialysate of latex.

Gorter, K. (11) 1.5% quebrachite, calculated on the latex, found in the latex or 50% of the total solids in the serum.

Jong, A. W. K. de. (2) After coagulating Hevea latex with alcohol, quebrachite was isolated in the solution.

Pickles, S. S. & Whitfield, B. W. (1) Quebrachite was isolated in the aqueous portion of the latex after coagulation.

Spoon, W. (5) Presence in latex.

Stevens, H. P. (13) Retards the rate of cure of protein free R.

de Vries, O. (24) p. 22. The amount of quebrachite in latex is nearly constant at 1.5%.

**Quinine.**

Eaton, B. J. & Bishop, R. O. (1) See Quinoidine.

Spence, D. (28) R.-100, S-8, quinine-1. Cure 25 min./40 lbs.

Twiss, D. F. & Brazier, S. A. (1) Mentioned.

**Quinoidine.**

Eaton, B. J. & Bishop, R. O. (1) Quinine cinchonine, cinchonidine and quinoidine are fairly powerful accels. The first three are identical in curing power and more active than quinoidine. ZnO accelerates their action.

Rosenbaum, J. L. (1).

Twiss, D. F. (12).

Twiss, D. F. & Brazier, S. A. (1).

**Quinol.**

Badische Co. (1) & (9) See Ageing-Oxidation.

**Quinoline.**

Anon. (84) An accel.

Bayer & Co. (5) Not an accel. (13) Mentioned.

Blanc, M. le & Kröger, M. (1) See Peachey process and Viscosity.

Ditmar, R. (62) Not a very good accel.

Dubosc, A. (40) Describes the free base, its sulfonate and hydroxy derivative. See Quinosol.

Eaton, B. J. (8).

Gottlob, K. O. (7).

King, A. H. (1) Suggests that salts of the sulfonate will be better accels. than the free acid.

Ostwald, Wa. (1) Used in 1908 to prevent the ageing or hardening of R. 2% added to latex.

Ostwald, Wo. & Ostwald, Wa. (1) A preservative for R. goods. See Ageing.

Pearson, H. C. (1) p. 55.

Stevens, H. P. (36) See Enzymes. (67) CO<sub>2</sub> derivative of quinoline mentioned.

**Quinoline Sulfate.**

Anon. (84) An accel.

Ditmar, R. (62) An excellent accel.

Eaton, B. J. (8).

King, A. H. (1).

**Quinoline Sulfonate.**

Ditmar, R. (62) Gave a very porous undercured stock.

**Quinosol.** See Latex-preservatives.

Anon. (84). Used in footwear. The combined action of quinosol and PbO is greater than the sum of their individual action.

Ditmar, R. (62) A sulfur yellow crystalline powder which works well with PbO in a factis stock.

Dubosc, A. (62).

Eaton, B. J. (8).

Pearson, H. C. (1) p. 86.

Spence, D. (28).

Spoon, W. (1) Quinosol, 8-hydroxyquinoline, added to latex to prevent spotting or rust on sheet R. Inactive as an accel.

Stevens, H. P. (36) See Enzymes.

### **Radium Rays.**

Ditmar, R. (2) Action on R.

### **Red Lead.**

Bayer & Co. (34) Used with amine accels.

Breuil, P. (3) Hardens R. by oxidation.

Brooks, B. T. (1) p. 136.

Ditmar, R. (47) May cause spontaneous combustion of R. Should be used with caution or not at all.

King, A. H. (1) Oxidizes R.

Marzahn, R. (1) p. 85.

Ostromuiskenskii, I. (2).

Pearson, H. C. (1) p. 102.

Thacker, S. P. (1) Used in place of PbO for vulc of R. by nitro compounds.

Weber, C. O. (7) Hardens R. (61) p. 185.

### **Regenerated Rubber.** See Devulcanization.

Anon. (127) R. accels. are without marked action on reclaimed R. unless alkalis have been used.

Alexander, P. (7) The rapid vulc. of reclaimed R. is probably due to PbO. (8) Reclaiming is not devulcanization. Colloidal solutions of vulc. R. in alkali are coagulated by alcohol like latex.

Basler, J. (1) Reclaiming by oxidizing agents at 150-200° C. O<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, HNO<sub>3</sub>, nitrates, chlorates, permanganates, chromates and aromatic nitro-compounds.

Dunlop, R. Co. (1) Reclaiming R. by use of accels. Piperidine, thiocarbonyl, etc.

Griesheim-Elektron Chem. Fabr. (1) Regenerating R. by the use of H<sub>2</sub>.

Harries, C. (21) (26) (31) R. regenerated from its hydro halogenides.

Hutz, H. (1) R. regenerated by use of chlorhydrine. H<sub>2</sub>S is formed.

Kirchhof, F. (3) See Tetrabromide.

Pickles, S. S. (6) R. reclaimed by alkalis, is a moderate accel.

Weber, C. O. (19) Reclaiming is plasticizing and not devulcanization.

Xylos Rubber Co. (1) Use of aniline, toluidine or xylydine in the alkali process for reclaiming.

### **Resins.** See Natural accelerators.

Alexander, P. (2) Oxygen compounds in R.

Bary, P. (5) Separation of resins and S from vulc. R. by osmosis.

Beadle, C. & Stevens, H. P. (1) Acetone extraction retards vulc.

Berry, W. G. (1) See Gutta percha.

Bloom, D. (1) Acidity of R. resins.

Bourne, L. M. (1) Resin content of 62 rubbers. Of 2 samples of the same R. the one with lower resin content will give higher tensile and be more elastic.

Burghardt, C. A. (4) Raw R. contains 3% of an acidic resin (1883).

Chaplet, A. & Rousset, H. (1) Deresination increases tensile. Over 2-4% resin makes R. difficult to work. Resins cause brittleness.

Dietrich, K. (2) Analysis for R. resins.

Ditmar, R. (14) Action of resins on R. at elevated temp. (18) Resins promote oxidation and lower tensile. (39) Analysis and dry distillation of R. resins. They do not oxidize. (39) No oxygen is taken up when air is blown thru a boiling solution of resins from Borneo R. (40) A new balata resin. (60) See Gutta Percha.

Ditmar, R. & Wagner, A. (1) R. resins react with S. to form acetone insoluble products.

Dubosc, A. (3) Solubility of Jelutong resins. (13) Deresinated R. cannot be vulc.

Editorial. (3) Résumé.

Edwardoff, E. (1) Action of halogens on R. resins.

Fol, J. G. (1) Resin content of R. decreases slightly on vulc.

Frank, F. & Marckwald, E. (4) Effect of resins on tensile, stickiness and milling properties.

Frank, F., Marckwald, E. & Liebschutz,

- J. (1) The odor of R. is due to resins.
- Harries, C. (13) R. resins give ozonides insoluble in  $\text{CHCl}_3$  and  $\text{CCl}_4$ .
- Heurn, F. C. van. (3) Extraction of resins retards vulc.
- Heuser, E. & Boedeker, G. (1) Emulsification of unsaponifiable R. resins in rosin soaps.
- Hillen, G. H. (1) Jelutong or Pontianac resins consist of lupeol acetate, amyrin acetate and a resene. Resin of Manihot R. is amorphous ischolesterol acetate and a balsam-like resin.
- Hinrichsen, F. W. & Kindscher, E. (2) Optical activity as a test for the quality of R. (9) Resins function as catalysts during vulc.
- Hinrichsen, F. W. & Marcusson, J. (1) Resins are optically active when resulting from the decomposition of R. Resins are not wholly derived from R. The acetone soluble oxidation products of R. are optically active.
- Hinrichsen, F. W., Marcusson, J. & Quensell, H. (1) Optical activity of resins from various Rs.
- Jacobson, F. (1) Extensive compilation of data on resins from various Rs. and gutta percha. Source, composition and nature. Rôle in vulc. Composition of latex and theory of coag. Bibliography.
- Jones, W. (1) Vulc. does not increase the acetone extract.
- King, A. H. (5) Resins protect from oxidation and aid in vulc. Their presence or absence has little effect on the time of vulc. if org. accels. are used.
- Klages, A. (1) Some R. resins are optically active. They are unsaturated and react with S and nitrous acid. Deresinated R. gives a better vulcanizate.
- Klassert, M. (1) Physical and chemical properties of R. resins.
- Lascelles-Scott, W. (1) See Latex. (3) R. resins probably consist of abietic acid or a similar body.
- Lobry de Bruyn, C. A. (2) Resistance of various Rs. to oxidation due to difference of the nature of the resins.
- Lobry de Bruyn, C. A. & Lent, F. H. van. (1) Amount of resin in R. has no relation to the durability of the vulc. R.
- Lock, R. H. & Bamber, M. K. (1) Effect of tapping on resin content of R.
- Marckwald, E., Frank, F. & Liebschutz, J. (1) Removal of resins increases tensile.
- Ostromuiskenskii, I. (11) Resins retard vulc. of R. by benzoyl peroxide.
- Potts, H. E. (4) Effect of resins on vulc.
- Rossem, A. van. (3) 25% of the resins from crepe, sheet or Para R. is unsaponifiable. Not all N is present in R. as protein. (4) Percent of resins, proteins and N in crude R. (6) Resins accelerate vulc. but are not essential. They lower tensile strength.
- Sahlfield, F. (1) See Gutta Percha.
- Schidrowitz, P. & Kaye, F. (1).
- Schon & Son. (1) See Rubber-Purification.
- Schulze, E. (1) Resins exert an oxidizing action on R. and combine with S and  $\text{S}_2\text{Cl}_2$ . (3) Resins promote the oxidation of R.
- Seidl, E. (4) Effect of resins on the S coefficient. Resins cause PbO to react with S. Resins and S give an exothermic reaction.
- Skellon, H. (1) Elimination of resins increases strength, decreases coefficient of vulc., and causes the R. to age poorly.
- Smith, S. (1) Resins reduce the amount of S available for vulc. and act as solvents for R. at vulc. temp.
- Stevens, H. P. (73) Effect of resins on quality, viscosity, etc.
- Strunk, H. (1) See Ageing-Oxidation.
- Terry, H. L. (1) Smoking R. produces soft resins mixed with phenolic compounds. Value of R. is inversely proportional to amount of resin.
- Tschirch, A. (1) Résumé of researches on the constitution of R.
- Tschirch, A. & Schereschewski, E. (1) See Balata.
- Ultee, A. J. (6) Treatise on R. resins (1915)
- Vaubel, W. & Diller. (1) Studies on R. resins.
- Wagner, A. (2) Properties of wild R. resins.
- Weber, C. O. (11) R. resins react with S during vulc. (34) Resins are not



- harmful if S. ratio is properly controlled. Soft resins cause bloom. Hard resins prevent it. (47) Resins and coefficient of vulc.
- Weber, L. E. (2) Effect of resins on the vulc. of R. mixes containing PbO. (3) Decrease of resin content during vulc. caused by metallic oxides forming acetone insoluble resins.
- Whitby, G. S. (2) Resin content of raw R. increases on deterioration. (8) p. 91. Removal of resins has little effect on the vulc. of a R-S mix. Resins accelerate the action of PbO.
- Whitby, G. S. & Dolid, J. (1) Studies on Hevea resin.
- Wilderman, M. (2) Resins are oxidized products of R. polyprene, are unstable and cause deterioration. They prevent correct vulc. of the R.
- Zilchert, P. (1) Rate of extraction of resins from 17 brands of R.
- Resorcin.**
- Badische Co. (1). (9) See Ageing-Oxidation.
- Bayer & Co. (41) See Ageing-Tackiness.
- Rhodamine (B).**
- Gaisman, L. & Rosenbaum, J. L. (1) An accel.
- Rubber-Miscellaneous.**
- Anon. (141) R. crumbles readily at the temp. of liquid air.
- Arens, P. (2) Smoking at 55° C. gives higher quality than air drying.
- Beadle, C. & Stevens, H. P. (4) Effect of mineral ingredients on the properties of R. (6) Valuation of crude R. (7) Effect of reworking R. (11) Insoluble portion of R.
- Bruni, G. (3) From the solubility of azobenzene, naphthalene and p-toluidine in R. it is shown that such systems are 2 component systems with the R. acting as a solvent forming true saturated solutions.
- Calvert, C. (1) Properties and vulc. of R. and gutta percha.
- Camille, A. (15) R. is softened by maceration in an alkaline solution.
- Chandler, C. F. (2) Properties of latex and R.
- Eaton, B. J. (27) Hevea Confusa R. is softer and stickier than Hevea R. altho it contains less resin.
- Frank, F. & Marckwald, E. (3) Vulc. studies on 32 samples of wild R.
- Geer, W. C. (5) p. 5. Origin of the name "Rubber."
- Henriques, R. (7) Properties of R.
- Herbst, E. (3) p. 339. Résumé of literature prior to 1907 on drying R.
- Höhnel, F. v. (1) R. divided into 8 classes according to method of preparation.
- Ilcken, C. A. & Down, St. V. B. (1) Inferior or scrap R. soaked in Na or K. thiosulfate, sulfite or hydro-sulfite and then in methylated spirit or benzene.
- Netherlands Government. (4) Comparison of acid coag. R. and evaporated preserved latex. Dialyzed and not dialyzed.
- Pearson, H. C. (1) p. 52. Cause of color in R.
- Reiche, H. v. (1) The m.p. of R. is usually about 200-220° C.
- Schidrowitz, P. & Goldsbrough, H. A. (8) Comparison of smoked sheet and pale crepe.
- Scott, J. (1) Examination of R. under the microscope.
- Stevens, H. P. (58) No relation between ease of "breaking down" R. and the ease with which R. takes up dry pigments during milling.
- deVries, O. (9) Cold milling does not affect the quality of R.
- Weber, L. E. (8) Comparison of plantation R. with German synth. R.
- Williams, W. A. (1) Advantages and defects of plantation R.
- Rubber-Purification.**
- Caspari, W. A. (5) Separation of soluble and insoluble constituents of R. and their properties.
- General caoutchouc Co., Ltd. (1) R. in an organic solvent treated with a non-rubber solvent which will extract the resin.
- Gerard, G. E. M. (1) R. solutions purified by sedimentation and skimming.
- Heim, F. & Marquis, R. (1) Pure R. is white and oxidizes readily in air.
- Pummerer, R. & Burghard, P. A. (1) Extraction of both proteins and resins from R. in a soxhlet extractor by use of mixed solvents.

- Scholz, V. (1) Pure R. and gutta percha by extraction with phenols or acid constituents of tar.
- Schön & Son. (1) Aniline, its homologues or derivatives as resin solvents. Alkalies or alkaline earths are also added to extract albuminous, mucous and coloring matters.
- Staudinger, H. & Fritsch, J. (1) Wilderman's method of purification of R. deVries, O. (24) p. 189. Obtained R. free from albuminous matter by adding HCHO and boiling in a solution of  $\text{Na}_2\text{SO}_4$ .
- Rubber Hydrochloride.** See Hydrochloric Acid.
- Rubber Glass.**
- Anon. (103) Vulcanized by the Peachey process.
- Jones, F. (3) R. glass and its possibilities.
- Rubber Research.**
- Dunstan, W. R. (3) Chemical problems concerning R.
- King, A. H. (4) Need for research on accurate physical testing methods.
- Porritt, B. D. (1) Scientific needs of the R. industry.
- Torrey, J. (6) Chemical and physical problems of the R. manufacturer.
- Twiss, D. F. & Brazier, S. A. (2) Small scale vulc. apparatus for research vulc. studies.
- deVries, O. (2) Research needed on coagulants, preservatives for latex and the preparation of R.
- Weber, C. O. (32) Importance of chemistry in the R. industry.
- Weber, L. E. (1) Preparation of R. mixes for research studies.
- Rubber-Structure and Chemistry.**
- Anon. (137) The unsaturated nature of R. and its constitution. (195) Molecular formula for R. (265) Bibliography on plantation R.
- Barrows, F. E. (1) & (2) Review on constitution of R.
- Bary, P. (1) Molecular wt. of R. is about 2720 at vulc. temp.
- Boswell, M. C. (1) Formulae for R. containing no double bonds.
- Breuil, P. (11) Structure of R.
- Cloez, S. & Girard, A. (1) R. contains S, P and Cl compounds as shown by dry distillation. The S is in the protein. The others are inorg. salts.
- Degin, A. (1) The ratio of H to O in R. is from 1:1.517 to 1.168.
- Ditmar, R. (8) R. is a highly polymerized terpene but does not give Riban's test for terpenes until after heating.
- Dubosc, A. (12) Favors the structural theories of Harries and Barrows. (46) Chemistry of R.
- Gladstone, J. H. (1) Predicted (1886) two pairs of doubly linked C atoms in R.
- Harries, C. (9). (10). (18). (25). (31) p. 224. Extensive résumé on constitution of R. and gutta percha. 1919. (22) First chemical evidence of an eight carbon ring. (23) Proof of the identity of natural and isoprene R.
- Herbst, E. (3) p. 304-311. Résumé of literature on constitution. 1911.
- Kirchhof, F. (10) Para R. is  $\text{C}_{10}\text{H}_{17}$ . Congo R. is  $\text{C}_7\text{H}_{14}$ . Structural formula proposed. (11) Spiral structure of the R. molecule from data on hydrogenation and the action of sulfuric acid.
- Klages, A. (1) Chemistry and preparation of R.
- Lieschütz, J. (1) Resin and ash of Congo R.
- Luff, B. D. W. (2) Review.
- Luftstein. (1) Composition of crude and vulc. R. and its determination by its derivatives.
- Marzahn, R. (2) Review. 1911-1914. (3) Review of R. chemistry for the 30 years prior to 1911.
- Olivier, S. C. J. (1) Review on structure and synthesis of R.
- Payen, M. (1) Constituents of natural R.
- Perkin, F. M. (1) Review on constitution and synthesis of R.
- Pickles, S. S. (1) Reactions of R. and structure of the molecule. (2) R. is composed of long chains of  $\text{C}_6\text{H}_8$ . Oxidation data requires that the chains be linked to form rings. (3) Closed chain formula for R. R. can be oxidized entirely to laevulinic acid and aldehyde.
- Rutgers, A. A. L. (1) Bibliography on plantation R.

- Schidrowitz, P. (8) Résumé of coagulation, chemistry, testing and analysis of R.
- Stewart, A. W. (1) p. 103. Chapter on rubber chemistry. Review of Harries and Pickles.
- Szelinski. (1) Lecture.
- Tschirch, A. (5) Constituents of R., gutta percha, balata and chicle.
- Weber, C. O. (33) The R. hydrocarbon is an aliphatic or olefinic open chain compound. Review of literature. (55) R. is a complex polyterpene.
- Whitby, G. S. (9) Review of Harries' work on constitution of R.
- Willstätter, R. & Veraguth, H. (1) R. is a polymerized cyclooctadiene.
- Rubber Seed Pulp.**  
General Rubber Co. (8) The ground pulp is emulsified before adding to R. or latex. Accelerates vulc.
- Rubber Solvents.** See **Solvents.**
- Rustiness.** (in rubber)  
Anon. (263) Prevention in Sheet R.
- Arens, P. (3) Caused by serum coming to the surface during drying. Prevented by soaking in water. See Sodium Bisulfite.
- Eaton, B. J. (7). (26) Rustiness is a crust of oxidized serum and contains 60% protein. Has no effect on the quality of the R. Prevented by soaking prior to smoking.
- Hellendoorn, H. J. (1) Inhibited by HCHO, bisulfite or rapid drying.
- O'Brien, T. E. H. (1) Rust formed by growth of micro-organisms is prevented by keeping the R. dry.
- Spoon, W. (1) See Quinosol.
- deVries, O. (24) p. 380.
- deVries, O. & Hellendoorn, H. J. (3) Aërobic micro-organisms acting on serum cause rustiness.
- Whitby, G. S. (8) p. 176. Cause and prevention.
- Saccharic Acid.**  
Gorter, K. (5) Found in latex of *Ficus Elastica*.
- Safranine.**  
Gaisman, L. & Rosenbaum, J. L. (1) An accel.
- Sandarac.**  
Hutin, A. (1) See Shellac.
- Salicylic Acid.**  
Anon. (99) See Latex-Preservatives.
- Billbrough, C. F. S. (1) See Latex-Preservatives.
- Sawdust.**  
Dubosc, A. (40) Reacts with S at 160° C. forming H<sub>2</sub>S. It is therefore an accel. of vulc. Bran and starch act the same.
- Scorching.** (Burning).  
Gibbons, W. A. (3) Premature vulc. with accels. prevented by maintaining R. in a softened condition.
- Harrison, M. M. & Morton, H. A. (1) See Dimethylamine dimethyl-dithiocarbamate.
- Repony, D. (1) S lubricated with oils is incorporated into R. mixes after all other materials have been added, to prevent "scorching."
- Rubber Service Laboratories. (1) See Thiocarbamilide.
- Selenium.** (Se)  
Ancel. (1) Use in R., glass, etc.
- Anon. (298) Vulc. of R. with Se.
- Boggs, C. R. (1) (2) (3) Se will vulc. R. at 150° C. which is much lower than its m.p. 217° C. Org. accels. function with Se the same as with S. (4) R-100, Se-14; Accelerene-1, PbO-25, ZnO and Whiting-175. Cure 1 hr./275° C.
- Ditmar, R. (7) 16% Se in R. gives a deep red color due to colloidal condition. No vulc. in 3 hrs./80° C. (62) Se is without effect as a vulc. agent.
- Elmer, W. (1) Vulc. of R. in CS<sub>2</sub> solution by pouring in liquified Se, applying pressure and heat at 149° C.
- Klopstock, H. (1) Vulc. of R. by halides of Se or Te.
- Marcy, E. E. (4) R-100, Se-20 to 100. Vulc. by application of heat (1854).
- Smith, H. E. (1) See Tellurium.
- Tassilly, E. (1) p. 94.
- Zsigmondy, R. & Spear, E. B. (1) Se does not give a satisfactory vulc. of R.
- Selenium Oxychloride.**  
Lenher, V. (1) A solvent for both crude and vulc. R.
- Serum.** See Proteins, Resins, Rustiness.
- Sesquisulfide of Antimony.** Sb<sub>2</sub>S<sub>3</sub>. See Antimony Sulfide.

**Shellac.**

- Anon. (105) Shellac in rubber compounding.  
 Goodyear, N. (1) Used as an ingredient in ebonite in 1851. See Ebonite.  
 Hutin, A. (1) Shellac retards ebonite cures but this action is nullified if it is reacted on with S before compounding. Copal and sandarac act the same.  
 Weise, W. P. (1) Use of R., shellac and varnish resins.

**Shrinkage Spots.**

- Ditmar, R. & Thieben, R. (2) See Colloid Chemistry of Rubber.

**Silicofluorides.** See Sodium Silicofluoride and Latex-Coagulants.**Slab Rubber.** See Variability.

- Eaton, B. J. (6) Soaking slab R. in soda gives a marked increase in rate of cure. (20) Wormed slab is slower curing than washed and dried samples. Excess acetic acid and  $\text{NaHSO}_3$  have small retarding effect. Creping and washing slab does not reduce the rate of cure. (26) Slab R. contains a maximum amount of natural accel.  
 Stevens, H. P. (27) Slab R. is not as uniform in rate of cure as pale crepe. Both aerobic and anaerobic fermentation produce natural accels. (37) Slab R. does not show the uniformity claimed by Eaton. (56) Crepe from slab R. is more variable than ordinary crepe. Advantages and disadvantages of slab R. (70) Tests on slab R. with and without  $\text{ZnO}$  and  $\text{PbO}$ .

**Smoking rubber.** See Variability.**Soap.** See Sodium Oleate.**Sodamide.**

- Anon. (84) An accel.  
 Bayer & Co. (7) (19) R-100, S-10, Accel.-1. Cure 30 min./3 atm.  
 Ditmar, R. (62).  
 Dubosc, A. (40).  
 Eaton, B. J. (8).  
 King, A. H. (1).  
 Twiss, D. F. & Brazier, S. A. (1).

**Sodium (Potassium).**

- Dubosc, A. (40) Compounded into R. as a paraffinated powder.

- Murrill, P. I. (1) See Sulfur chloride.  
 Ostromuiskenskii, I. (21) (25) Na dissolved in alcohol used with nitro compounds to improve ageing.  
 Spence, D. (27) Devulc. of R.  
 Spence, D. & Russel, W. F. (1) Improvement of low grade R. by use of Na.  
 Twiss, D. F. (7) Na or K dissolved in primary or secondary amines such as aniline or diphenyl amine for acceleration of vulc.  
 Twiss, D. F. & Brazier, S. A. (1).

**Sodium Acetate.**

- Eaton, B. J. (3)  $\text{NaOAc}$  reduces the coag. effect of  $\text{HCl}$  on latex.  
 deVries, O. (15) & (24) p. 101. Added to latex gives faster curing R. Increases rate of drying. Soaking R. in an aqueous solution of, increases rate of cure.

**Sodium Bisulfite.** See Latex-Preservatives and Sulfites.

- Anon. (262) & (266) Causes no change in tensile strength when added to latex but slight decrease in rates of cure.  
 Arens, P. (3)  $\text{NaHSO}_3$  does not prevent rustiness.  
 Barrowcliff, M. (3) The use of  $\text{NaHSO}_3$  was first published by Barrowcliff. Slower drying of R. prepared with  $\text{NaHSO}_3$  is due to sodium acetate formed.  
 Beadle, C. & Stevens, H. P. (15) Acts as an antiseptic in small amounts in the latex and destroys coloring matter by bleaching. Quality of R. is undiminished.  
 Beadle, C., Stevens, H. P. & Morgan, S. (1) Prevents surface darkening of R. Does not affect the quality of the R.  
 Campbell, L. E. (4)  $\text{NaHSO}_3$  added to latex cause no change in tensile strength, but a slight decrease in rate of cure.  
 Cayla, V. (8) Used to bleach R. (11) Arguments for and against the use of  $\text{NaHSO}_3$ .  
 Day, F. W. F. (1) Oxidation of R. is considerably reduced by adding  $\text{NaHSO}_3$  to the latex.  
 Dubosc, A. (22)  $\text{NaHSO}_3$  in small amounts does not kill the enzymes but the coloring matter is destroyed

by  $\text{H}_2\text{SO}_4$  which is liberated by acid during coagulation.

Eaton, B. J. (9) Has a slight retarding action during vulc. (20) See Natural Accelerators.

Eaton, B. J. & Grantham, J. (4) (5) No effect on tensile strength and rate of cure. Retards process of maturation because of disinfecting action.

Fölsing. (1)  $\text{NaHSO}_3$  or  $\text{H}_2\text{SO}_3$  added to a solution of R. to bleach it.

Heilbronner, A. (1) See Tannin.

Morgan, S. (1) p. 64.  $\text{NaHSO}_3$  prevents spotting and bleaches the R. See Ageing-Oxidation.

Rossem, A. van. (6) Inactive in the vulc. of R.

Sharples, A. (1) See Enzymes.

Stevens, H. P. (19)  $\text{NaHSO}_3$  inhibits the action of the oxidase in latex and prevents darkening of the rubber. There is no appreciable effect on quality of the R. (62) A slight retardant of cure when added to latex but gives satisfactory tensile tests on the R. (82) Used to produce R. of paler and more uniform quality. Inferiority of crepe R. as compared with sheet R. is due to machining of freshly coagulated latex.

Ultee, A. J. (2) (11) Effect of bleaching agents on the quality of the R. (3) Preparation of light colored R. (4) There is no increase of ash in R. by addition of  $\text{NaHSO}_3$  to latex, therefore Na Acetate is not left in the R. to cause slower curing.

deVries, O. (15) Direct effect of  $\text{NaHSO}_3$  is to improve all the qualities of the R. (24) p. 30.  $\text{NaHSO}_3$  acts as an anti-oxidant but not as a bleaching agent. p. 94. Acts more strongly against oxidation than  $\text{Na}_2\text{SO}_3$ . Immersion of coagulum in  $\text{NaHSO}_3$  may cause slight retardation in cure.

Williams, W. A. (1) 0.25%  $\text{NaHSO}_3$  increases time of cure 27%. 3% entirely prevents complete vulc.

**Sodium carbonate.** See Latex-Preservatives.

Beadle, C. & Stevens, H. P. (16) Accelerates vulc. but the compound ages poorly.

Eaton, B. J. (9) Coagulum soaked in  $\text{NaOH}$  or  $\text{Na}_2\text{CO}_3$  cures rapidly, but

becomes tacky and ages poorly. (16)

Added to coagulating bath gives acceleration of vulc. to the resulting R.

Pickles, S. S. (1) An accel. of vulc.

Rossem, A. van. (6) Comparison of various alkalis as accels. by their coefficient of vulc.  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$ .

Schidrowitz, P., Feldenheimer, W. & Plowman, W. W. (1) Clay is treated with  $\text{Na}_2\text{CO}_3$  before compounding into R.

Shirai, S., Tanaka, S. & Yoshikawa, B. (1) R. is heated with an equal wt. of  $\text{Na}_2\text{CO}_3$  in absence of S for the manufacture of vessels to contain food.

**Sodium Chloride.** See Latex-Coagulants.

Ditmar, R. (36) Traces of  $\text{NaCl}$  or other chlorides are harmful in hot air cures using  $\text{PbO}$ . Not so in steam cures. R. takes up chlorides from the wash water.  $\text{MgCl}_2$  is injurious to R.

**Sodium Cresylate.**

Davidson, S. C. See Latex-Preservatives.

General Rubber Co. See Latex-Preservatives.

**Sodium Fluoride.**

Anon. (99) See Latex-Preservatives.

General Rubber Co. (3) See Latex Preservatives.

Sandman, D. (1) See Latex-Coagulants-Hydrofluoric acid.

**Sodium Hydroxide.** See Potassium Hydroxide, Alkalies and Sodium Phenolate.

Badische Co. (7) An accel. in synth. R.

Bayer & Co. (15) Used in preparation of synth. R. and left in to act as an accel. (42) See Aniline.

Beadle, C. & Stevens, H. P. (16) An accel. which causes poor ageing.

Dubosc, A. (40).

Eaton, B. J. (6) Coagulum treated with caustic gives rapid vulc. in the R. (9) Alkalies are powerful accels. but produce tackiness.

Editorial. (1) Warning to R. growers against the use of caustic.

Esch, W. (16) Mixture of caustic and  $\text{MgO}$  as an accel.

Martin, W. G. (1) 0.5% of caustic is an accel. 5.0% retards vulc.

- Meyer, E. E. A. G. (2) Concentrated solution of caustic as an accel.
- Pickles, S. S. (4) As an accel. should only be used in small amounts.
- Porritt, B. D. (1).
- Twiss, D. F. (2) (4) (12) Caustic in glycerine is dehydrated and is an accel. which gives good ageing.
- Twiss, D. F. & Howson, C. W. H. (1) See curves in cures using caustic as an accel.
- Richards, Taylor & Wylde. (1) See Sodium Sulfide.
- Schidrowitz, Feldenheimer & Plowman. (2) Caustic dispersed on clay as an accel.
- Sodium Oleate.**
- Schidrowitz, Feldenheimer & Plowman. (2) Mixed with clay as an accel.
- Spence, D. (28).
- Sodium Perborate.**
- Bernstein, G. (6) See Lead Sulfide.
- Sodium Peroxide.**
- Dubosc, A. (40).
- Gawalosk, A. (1) See Solvents for Rubber.
- Seidl, E. (1) An accel. similar to PbO.
- Sodium Phenolate (Cresolate or Naphtholate).** See Latex-Preservatives.
- North British Rubber Co. (1) Alkali dissolved in phenols, cresols or etc. as accels.
- Pickles, S. S. (1).
- Porritt, B. D. (1).
- Twiss, D. F. (6).
- Twiss, D. F. & Brazier, S. A. (1).
- Sodium Silicofluoride.** See Latex-Coagulants.
- Stevens, H. P. (62) (68) Used as a mold preventative for R. (75) Ageing of R. prepared by use of silicofluorides. Variations of cure caused by the same are obliterated in a PbO stock. (76) Modified application of. (79) Vulc. R. coagulated with sodium silicofluoride ages as well as standard R. Excess of the reagent does not accelerate ageing. (80) (83) Mold prevention.
- Sodium-Sulfite.** See Latex-Preservatives.
- Anon. (157) See Sulfur-Bloom. (162) Used for removal of S bloom.
- Davidson, S. C. (9) Acetic acid added to latex containing  $\text{Na}_2\text{SO}_3$  generates  $\text{H}_2\text{SO}_3$  which prevents growth of micro-organisms and formation of air blisters.
- Falke, O. & Richards, A. C. (1) Vulc. R. with antimony sulfides and  $\text{Na}_2\text{SO}_3$  at  $275^\circ \text{F}$ .
- Heilbronner, A. (1) See Tannin.
- Ultee, A. J. (9) Used as a bleaching agent.
- deVries, O. (3) Good vulc. results with R. from latex treated with  $\text{Na}_2\text{SO}_3$ .
- Sodium Thiosulfate.**
- Davidson, S. C. (1) See Latex.
- Ultee, A. J. (6) Decreases the viscosity of the latex. Its anti-oxidizing effect is not so strong as the bisulfite.
- de Vries, O. (15) & (24) p. 99. Added to latex causes slight decrease in rate of cure and viscosity.
- Sodium Sulfide.**
- Sodium Polysulfide.** See Potassium Sulfide.
- Davidson, S. C. (3) See Latex-Coagulation.
- Dubosc, A. (6) See Gerard, A. (1).
- Gerard, A. (1) Vulc. of R. in a  $25^\circ \text{Be}$ . solution of "liver of S" followed by baking at  $138^\circ \text{C}$ . Boiling  $\text{Na}_2\text{S}_x$  solution destroys tackiness in R.
- Hancock, T. (1) Alkali sulfides used in R.
- Hoffer, R. (1) See Gerard, A. (1).
- Moulton, S. (2).
- Pickles, S. S. (4)  $\text{Na}_2\text{S}_x$  will vulc. R. without free S.
- Price, R. B. (1) Impregnation of fabric with  $\text{Na}_2\text{S}_x$  to increase union with R. See Thiocarbaniide.
- Richards, Taylor & Wylde. (1) Vulc. of R. in 1850 by submersion in an alkaline suspension of S.
- Rodier, P. (1) See Chlorine.
- Rossem, A. van. (6) See Sodium Carbonate.
- Schidrowitz, P. (52) See Latex-Vulcanization.
- Terry, H. L. (3) Could not reproduce Gerard's process.
- Sodium thiosulfate.**
- Davidson, S. C. (1) (2) See Latex-Preservatives.
- Sodium Xanthates.** See Xanthates.

**Softeners for Rubber.**

Aultman, P. M. & North, C. O. (1) Action of softeners on raw and vulc. R.

“Solarization.” See Acetone Peroxide and Light.

Buir, H. W. (1) Vulc. of R. by artificial light is an improvement over use of sun's rays.

**Solvents for rubber.** See Colloid Chemistry of Rubber.

Anon. (11) Use of coal tar distillate as a R. solvent by Prof. Syme. (1818). (187) Solution of R. in solvents is accelerated by essential oils such as eucalyptus, thyme or citron oil. (284) Dichlorethylene or homologues as R. solvents, non-inflammable and chemically inert. Non-poisonous and without narcotic action.

Aufrecht, A. & Jacobson, F. (1) Early history of R. solvents. R. is soluble in nut oil, Dippel's oil, rectified ether, turpentine, drying oils, rectified petroleum, coal tar, SO<sub>2</sub> in camphor, melted naphthalene and camphor. Ammonia emulsifies R. Later R. solvents include pyridine, benzol, shale oil, CS<sub>2</sub>, CHCl<sub>3</sub>, CCl<sub>4</sub> and chlorine derivatives of acetylene.

Axelrod, S. (3) Solubility of various wild and plantation rubbers in benzene.

Barus, C. (1) Vulc. soft R. or ebonite dissolves in CS<sub>2</sub>, C<sub>6</sub>H<sub>6</sub>, aniline, CHCl<sub>3</sub>, CCl<sub>4</sub>, etc., when heated to 200° C. Vulc. of a solution of R. to a liquid ebonite with 20% S at 185°-210° C. This solution hardens to a jet black enamel.

Beiersdorf, P. (1) R. is soluble in ether in presence of oleic acid.

Berniard, R. (1) Alcohol precipitates R. from a solution in oil of aspic. (1781).

Caspari, W. A. (4) Osmotic pressure determinations of R. in benzene show that the osmotic rise increases faster than the conc. Old solutions give lower pressure than fresh, as viscosity decreases the sol phase diminishes. Lower pressure due to sol and gel phases in R.

Condamine, C. M. (1) Fresnau found elastic resin insoluble in alcohol and

water but soluble in nut oil on slight warming.

Ditmar, R. (8) See Colloid Chemistry. Esch, W. & Chwolles, A. (2) Ether dissolves an appreciable amount of R.

Fabroni. (1) Used rectified petroleum as a solvent for R. (1792).

Fendler, G. & Kuhn, O. (1) Solubility of R. in cold solvents is incomplete and varies with time and temp.

Fischer, E. (1) Dichlorethylene as a R. solvent has the following advantages: rapid in action, low boiling, non-inflammable and low specific gravity.

Flusin, G. (1) Organic liquids absorbed by vulc. R. fall into two classes, those that are quickly absorbed and those like water, where an appreciable weight increase is obtained only after several hours.

Fourcroy, A. F. (1) Coating silk with R. solutions. (2) R. is soluble in turpentine and ether. See Latex.

Fourcroy, A. F. & Nicholson, W. (1) Oil of lavender and turpentine as R. solvents.

Gassicourt, C. de. (1) R. soluble in ether and alcohol.

Gawalosk, A. (1) Para R. swelled in linseed oil, linseed oil varnish and linseed oil fatty acids is treated with HNO<sub>3</sub>, Na<sub>2</sub>O<sub>2</sub>, Ca<sub>2</sub>O<sub>2</sub> or BaO<sub>2</sub>. The first two give flexible goods, the latter two are harder.

Gottlob, K. & Miksch, K. (1) Fresh R. is soluble in ether. After drying it becomes insoluble.

Grossart, C. (1) Drying oils used as solvents.

Hanausek, T. F. (1) Solubility of various rubbers in ether, turpentine, CHCl<sub>3</sub>, naphtha, benzene and CS<sub>2</sub>.

Harzford, E. N. (1) See Sulfur.

Herbst, E. (3) Lengthy abstract of Ditmar, R. (12) & (13). Data on swelling of R. in solvents.

Herissant & Macquer. (1) R. dissolves in Dippel's oil, terebenthene and rectified ether in vapor or solution.

Jong, A. W. K. de & Haas, T. de. (1) Castilloa R. contrary to C. O. Weber, is soluble in ether.

Kayser, R. (1) Solutions of R. in camphor oil miscible with varnishes and lacquers.

- Kletzinsky, V. (1) See Naphthalene.  
Kohlschütter, V. (1) Swelling of R. in solvents.  
Lascelles-Scott, W. (4) Ether was used as R. solvent in manufacture of the first gum tubing.  
Leonhardi, J. G. (1) Nut oil, ether and other solvents for R. (1781).  
Ludersdorf, F. (1) Sulfurated turpentine as a solvent for R. (2) First mixing of S into R. whereby stickiness was decreased.  
Mackintosh, Chas. (1) Use of coal tar naphtha as R. solvent (1823).  
Macquer. (1) Purified sulfuric ether used as a R. solvent.  
Montgomery, J. J. (1) Solution of vulc. R. in a petroleum oil boiling at 200° C. or higher.  
Ostwald, Wo. (1) Relation between swelling power of R. and the solvent.  
Payen, M. (1) Ether dissolves R.  
Pelletier, P. (1) Purified ether as a R. solvent. It is necessary to use ether which contains some moisture.  
Pfaff, C. H. (2) R. is insoluble in dry ether. It only swelled and softened in the hot vapors.  
Reichenbach. (1) Rectified Dippel's animal oil on slight warming dissolves R.  
Spence, D. & Kratz, G. D. (2) Effect of various solvents on R.  
Weber, C. O. (58) R. is not completely sol. in ether. Insoluble portion is variable and does not differ chemically from the soluble portion although it usually contains less oxygen.  
Weber, L. E. (5) Gasolene as a R. solvent. (6) Benzol, solvent naphtha, shale oil, CS<sub>2</sub> and CCl<sub>4</sub> as R. solvents. CS<sub>2</sub> is an excellent diluent for S<sub>2</sub>Cl<sub>2</sub>.  
Williams, H. J. (1) pt. VI. Naphtha as a R. solvent.
- Spiller's Resin.**  
Spiller, J. (1) See Ageing.
- Spontaneous Coagulation.** See Latex-Coagulation-Spontaneous.
- Spots.**  
**Spotting of Rubber.** See Enzymes, Colloid Chemistry of Rubber.
- Starch.**  
Dubosc, A. (23) (26) Reacts with S. at vulc. temp. to give H<sub>2</sub>S. (40) See Sawdust.  
Eaton, B. J. (23) Does not retard vulc.  
Stevens, H. P. (2) A poor substitute for protein in R.  
deVries, O. (24) p. 24. There is no starch in Hevea latex.
- Stearic Acid.**  
Mackintosh, J. G. & Boggett, J. W. (1) Paraffine and stearic acid as preservatives for R.  
Weber, L. E. (9) See Oleic Acid and Acids.
- Strontium Chromate.**  
Lascelles-Scott, W. (32) More stable than lead or zinc chromate. A good pigment.
- Strontium Oxide.**  
Gottlob, K. O. (7) Inactive as an accel.
- Strontium Thiosulfate.**  
Levinstein, E. (1) Vulc. of R. without S.
- Styrolene.**  
Matthews, F. E. (1) Use of polymerized styrolene in R.
- Sublimed White Lead.**  
Grove, J. M. (1) Has lower curing power than PbO, basic lead carbonate or sublimed blue lead.  
King, A. H. (1) Consists of 75%-PbSO<sub>4</sub>, 16% PbO and 5.5% ZnO. Has low curing power.  
Pearson, H. C. (1) p. 112.  
Simmons, H. E. (3).  
U. S. Publications. (1) Description of lead pigments.
- Substitute.** See Factis.
- Succinic Acid.**  
Harries, C. (29) Formed by action of ozone on R.
- Succinic Dialdehyde.**  
Harries, C. (19) (29) By action of ozone on R.
- Sugar.** See Latex-Coagulants.  
Bamber, M. K. (5) 0.36% sugar calculated as cane sugar in latex of a Hevea tree at Paradynia.



- Beadle, C. & Stevens, H. P. (5) 0.12% sugar in latex of 10 yr. old and 0.22% in a 4 yr. old tree calculated as glucose. (13) 0.15% to 0.24% sugars in dialysate of preserved latex after inversion.
- Spoon, W. (5) Presence in latex.
- Vernet, G. (14) 1.43% sugar in latex. (15) Latex of new trees may contain 3% sugar. Bacteria which attack sugar and proteins have been isolated in R.
- deVries, O. (24) p. 23. In addition to quebrachite, ordinary sugars not yet identified are present in latex.
- Whitby, G. S. (5) Some species of bacterium may produce fermentation when carbohydrates are present but putrefaction when they are absent. (7) Prevention of decomposition of proteins by sugars. See Enzymes.
- Sulfites.** See Lead Sulfite, Zinc Sulfite and Sodium Bisulfite.
- Moulton, S. (2) Vulc. of R. and gutta percha by S acids of a lower degree of oxidation than  $H_2SO_4$ , preferably by sulfites.
- Eaton, B. J. (24) Soaking coagulum in  $NaHSO_3$  prevents darkening of the R.
- Sulfocyanic Acid.**
- Dubosc, A. (13) S on R. protein at  $140^\circ C$ . gives HSCN and  $H_2S$ . (30) (40) (42) HSCN formed during vulc. of R. Its action is two fold. It adds on to double bonds, polymerizing the R. as well as decomposing into HCN and active S.
- Bedford, C. W. & Sebrell, L. B. (1) (2).
- Luff, B. D. W. (1) Found in R. cured by the aid of Hexa.
- Sulfonic acid derivative of Dinitro-dimethyl-benzoic Acid.**
- Parepa, M. C. D. (1) See Nitric Acid.
- Sulfoxy Quinoline.**
- Eaton, B. J. (8) Mentioned.
- Sulfur.**
- Ahrens, F. (1) Loss of S on ageing. See Hydrogen Sulfide. (6) Vulc. reverses on ageing as shown by an increase in acetone soluble S.
- Anon. (76) Relation of S to vulc. (121) Solubility of S in aniline and benzene. (134) Preparation of colloidal S. (164) Proper amount of S to add to R. Effect of excess. (222) Solubility of S in R. at various temps. and crystallization in various forms on cooling.
- Barus, C. (1) See Vulcanization in Solution.
- Bary, P. & Weydert, L. (1) Reversible character of vulc.
- Bernstein, G. (2) Theoretical.
- Blossom, T. M. (1) Abstract of Nelson Goodyear's first patent on ebonite.
- Breuil, P. (12) Properties of various forms of S. (16) Researches on vulc.
- Bysow, B. V. (3) Vulc. is entirely physical. R. & S give no rise in temp. at  $150^\circ C$ . At  $160^\circ C$ . the temp. rises quickly to  $225^\circ C$ . and  $H_2S$  is given off.
- Ditmar, R. (19) p. 94. List of over 300 patents related to the vulc. of R. (24) Effect of amount of S on the tensile strength of R. (26) Effect of amount of S on specific gravity. (35) Decomposition point of R. rises with the S content up to 25% and is also increased by  $MgO$ ,  $ZnO$  &  $PbO$ . Barytes or pitch are without effect. Factis up to 10% lowers the decomposition point.
- Dubosc, A. (17) Colloidal S does not accelerate vulc. (21) Analysis of vulc. R. for sulfides and sulfites. (42) Hexavalent S for explaining the mechanism of action of accels.
- Erdmann, H. (1) Melted S at  $160^\circ C$ . contains thiozone and a viscous polymeride of octatomic S. Vulcanite is mainly a thiozonide of R. containing S and polymerized cyclo-octadiene in solution.
- Esch, W. (5) Polemical with Luder-dorff (1).
- Fanshawe, J. A. (1) S admixed with R. in 1841.
- Fol, J. G. & Heurn, F. C. van. (1) Effect of time, temp. and amount of S.
- Goodyear, Chas. (2) First vulc. with S. (4) Vulc. of R. by S aided by the oxides or carbonates of lead.
- Hancock, T. (1) Patent on the vulc. of R. 1846. (2) Vulc. of R. by dipping in molten S and later heating for a short time at  $150^\circ C$ .

- Harzford, E. N. (1) Samuel Guthrie (New York) used S dissolved in turpentine as a R. solvent in 1831.
- Hayward, N. (1) Use of S to improve R. and cause it to dry more perfectly. (No vulc. by heat.)
- Heilbronner, A. & Bernstein, G. (1) No vulc. takes place unless the S is in solution in the R.
- Henriques, R. (4) Free S is necessary for good ageing. (9) Removal of S from unvulc. R.
- Hinrichsen, F. W. (9) R. & S combine slowly at ordinary temp. The reaction may be reversed.
- Hinrichsen, F. W. & Kindscher, E. (2) See Sulfur Chloride. (9) Theory of hot Vulc.
- Höhn, J. B. (1) There is no rise in temp. during vulc.
- Hübener, G. (2) Vulc. of R. in solution in naphthalene with determination of Sc.
- Jorissen, W. P. (1) Attributes the discovery of vulc. to Jan van Geuns in 1828. (2) Priority of Geuns defended.
- Kirchhof, F. (1) The function of S is catalytic and not the direct cause of vulc. (2) (7) S<sub>2</sub> or S<sub>8</sub> is responsible for vulc. and is removable by solvents. Atomic S acts at the double bonds and thereafter is not removable. Accels. change S<sub>2</sub> and S<sub>8</sub> to atomic S.
- Kissling, R. (1) The true vulcanizing substance, whether S or sulfides, has not been determined.
- Loewen, H. (1) Polemical with Spence & Scott (1). (2) S is more soluble in vulc. than in unvulc. R. S diffuses into warm R. Adsorption plays no part in vulc. The three stages of vulc. are fusion of S, solution in R. and chemical reaction.
- Ludersdorff, F. (1) Turpentine containing 3% of S as a solvent for R. On evaporation the R. so obtained is less tacky.
- Lumiere. (1) Preparation of colloidal S.
- Marckwald, E. & Frank, F. (11) History of vulc. processes and theories.
- Marzahn, R. (1) p. 417.
- Noyer. (1) Flowers of S are insoluble in CS<sub>2</sub>.
- Ostromuiskii, I. (25) A small amount of S is used in R. cured with nitro compounds to prevent ageing.
- Payen, M. (2) Heating R. in S at 116° C.
- Pickles, S. S. (6) High amounts of S cause R. to harden and deteriorate. Fine precipitated S cures faster than coarse flowers of S.
- Prins, H. J. (1) S may add on to two double bonds of two R. molecules and cause polymerization.
- Rimpel, H. (1) Crystallization of S on cooling vulc. R.
- Schidrowitz, P. (17) See Kirchhof (7). (46) Free S is a good preservative.
- Schulze, E. (3) Bloom preserves R. Effect of factis on ageing.
- Skellon, H. (1) Polyprene sulfide. (2) Mass action of S. (3) Migration of S and reaction with R.
- Spence, D. (21) A critical temp. between 65-80° C. where the velocity of vulc. suddenly increases. (22) Solubility of S in R.
- Stern, P. (2) Mechanism of the action of S.
- Stevens, H. P. (4) Determination of S as sulfides and sulfates in vulc. R. (73) Stability of vulc. R. Variation of the ratio of S to R. Reversion of the stress-strain curve.
- Thomson, W. (6) R. in molten S will absorb 50% without vulc.
- Twiss, D. F. (9) Relative activity of different forms of S. Bibliography. (10) Soluble S will vulc. R. faster than the insoluble form.
- Twiss, D. F. & Thomas, F. (1) "Mu" S, which is insoluble in CS<sub>2</sub> is less active at 98° C. than "gamma" S, which is soluble. At 148° C. there is little difference. Tests use aldehyde ammonia as the accel.
- Venable, C. S. & Green, C. D. (1) Solubility of S in R. increases with the degree of vulc. A stock with 4% Sc will be saturated with 15% free S at 140° C.
- deVries, O. & Hellendoorn, H. J. (2) Effect of time of cure on tensile and stress-strain curve.
- Weber, C. O. (49) S must be free from acid and be stored in a cool place to avoid oxidation. (54). (61) p. 176.
- Westhead. (1) Vulc. of R. by S vapors.

- Wiesner, J. (1) p. 388. History of vulc. with S.
- Williams, H. J. (1) Pt. IV. S, its manufacture and uses.
- Sulfur-Bloom.**
- Ahrens, P. (1) Cause of bloom.
- Anon. (22) Pure S bloom only found in R. free from resin. Resin also sweats out. Bloom reoccurs after removal but does not form under water. (68) R. vulc. with lead hyposulfite is nonblooming. (69) See Canada Balsam. (102) Factis retards bloom. (144) Asphalt, oils, tars, bitumens, paraffines and soft substances retard bloom. Discussion of control. Paraffine gives a blue waxy bloom. (157) Removal of bloom by  $\text{Na}_2\text{SO}_3$ . (160) Removal by caustic. (162) Removal by  $\text{NaHSO}_3$ . (210) See Wilhöft (1). (216) Bloom on red R. articles.
- Armstrong, J. M. (1) Removal from gutta percha by treatment with hydrogen.
- Bolas, T. (3) Zinc oxysulfate retards bloom.
- Chertoff, G. J. (1) See Ageing-Oxidation.
- Friswell, A. E. (1) Data on bloom.
- Gregory, G. F. (1) Review.
- Heinzerling, C. (3) Continued blooming causes R. to become hard and brittle.
- Marckwald, E. & Frank, F. (8) R. goods vulc. with  $\text{S}_2\text{Cl}_2$  will show a bloom of free S.
- Rimpel, H. (1) Sometimes the unstable form of S changes to the stable form inside the R. and the S collects in centers giving rise to mottling.
- Springer, G. (2) S dissolves in R. during mastication on hot rolls and crystallizes out again on cooling.
- Wilhöft, F. (1) Canada balsam, 1 part, and S, 2 parts, heated till it does not crystallize on cooling. Used for the production of nonblooming goods. (2) Degree of vulc. has no effect on bloom.
- Weber, C. O. (34) See Resins. (41) Vulc. with low S for a long time to avoid bloom. General discussion of bloom.
- Sulfur-Coefficient of Vulcanization.** (Sc.)
- Alexander, P. (11) Sc. cannot be removed without destruction of the R. molecule.
- Anon. (79) Vulc. forms a sulfide of R. Rate of reaction is a function of temp. and is increased by  $\text{PbO}$ ,  $\text{MgO}$  and  $\text{ZnO}$ . Pressure also increases the rate of cure, contrary to C. O. Weber but in agreement with J. Minder. (122) Casein increases Sc.
- Arens, F. (1) Sc decreases on ageing of low quality R.
- Axelrod, S. (1) Effect of mastication on Sc.
- Bary, P. (1) Equilibrium between R and S. (5) All free S is removed by acetone extraction.
- Bernstein, G. (3) See Depolymerization. (5) See Vulcanization.
- Blanc, M. le & Kröger, M. (1) Relation between viscosity and Sc.
- Bobet, R. (1) Vulc. R. contains only 1.5% Sc.
- Bourn, A. O. (3) Rate of combination of S with R. at ordinary temp. See Vulcanization at low temperatures.
- Bysow, B. V. (4) Curves for free and combined S.
- Camille, A. (7) In no case is more than 2.5% S chemically combined with the R. (21). (22) Résumé of early work on vulc. by S.
- Cranor, D. F. (1) R-100, S-6,  $\text{ZnO}$ -1. Cure at  $144^\circ\text{C}$ . Sc 2.85 ages better than 4.76. Hexa gives 2.83 Sc in 50 min., without hexa gives 2.85% Sc in 130 min. Dimethylammonium-dimethyldithiocarbamate gives 1.09, 1.21 & 1.45% Sc in 3, 4 & 5 min. Sc to give 700% elongation at 1000 lbs./sq. in.—Natural accels.—4.9%, hexa—1.8%, dithiocarbamate—0.9%.
- Ditmar, R. (24) Effect of S content on tearing properties. (49.) Résumé of data on Sc, mechanism of vulc., etc.
- Ditmar, R. & Wagner, A. (1).
- Donath, E. (1) Polemical with Heinzerling on Sc.
- Eaton, B. J. (5).
- Eaton, B. J. & Day, F. W. F. (2) R-100, S-10, cured at  $140^\circ\text{C}$ . Crepe gives 3.7 to 4.1% Sc for optimum cure. Slab gives 4.2 to 4.6%. Limits for Sc at optimum cure extended to 3.7-4.6%. Time vs. Sc

- gives a smooth curve. (4) Rate of cure and Sc.
- Esch, W. (4) See Magnesium Oxide.
- Fendler, G. & Kuhn, O. (1) Combined S is all retained in the bromide of R.
- Frank, F. (1) Sc refers to the amount of S in combination with 100 parts of R.
- Gottlob, K. O. (7) Org. accels. increase Sc.
- Guerry, L. (1) Sc is removed by heating vulc. R. to 180° C. with primary or secondary amines.
- Harries, C. & Fonrobert, E. (3) Desulfurization of vulc. R.
- Heil, A. & Esch, W. (1) p. 62. Vulc. by S can only take place at temps. above the melting point of S. Sheets of R. and S exposed to light show no Sc.
- Heilbronner, A. & Bernstein, G. (3) See Light.
- Heurn, F. C. (1) 37.04% Sc found in ebonite which is higher than the theoretical 32%.
- Hinrichsen, F. W. (3) Physical chemistry of R. (5) A sample of vulc. R. increased from 4.5% to 7.5% Sc in 6 months at ordinary temp.
- Hinrichsen, F. W. & Kindscher, E. (4) Theory of vulc. (5) Sc usually includes S as metallic sulfides.
- Hinrichsen, F. W. & Stern, R. (1) Study of Sc by vulc. of R. with S in solution in naphthalene.
- Heurn, F. C. van. (3) Sc in under-vulcanized R.
- Hübener, G. (4) (5) Quantitative data on Sc in ebonite. Mono- and disulfides of R.
- Iterson, G. van. (1) Résumé of Weber, Spence, Skellon, etc., on Sc.
- Kelly, W. J. (1) (2) Determination of true free and combined S.
- Kratz, G. D. & Flower, A. H. (1) Mass action of S. R. should not be evaluated solely on its Sc content. (2) No direct relationship between Sc and the state of cure as measured by physical properties. Quick curing with accels. gives correct cures with abnormally low Sc.
- Kratz, G. D., Flower, A. H. & Shapiro, B. J. (2) No relationship between physical properties and Sc in accelerated mixes.
- Loewen, H. (2) Solubility of S in R.
- Marckwald, E. & Frank, F. (4) Sc is not removable from R. without decomposition of the R.
- Martin, G. & Elliott, F. L. (1) Effect of resins and proteins on Sc. See Natural Accelerators.
- Minder, J. (2) Effect of time and temp. on vulc.
- North, C. O. (3) See Accelerators.
- Repony, D. (1) Nascent H or NaOH do not remove combined S. Zn dust and HCl on vulc. R. in kerosene removes some Sc.
- Rosenbaum, J. L. (1) 1% hexa in absence of ZnO shortens the cure to one third the time but gives a higher Sc than the unaccelerated mix.
- Rossem, A. van. (6) Effect of milling, washing, viscosity, S ratio, acidity, ash, fillers, accels., and condition of vulc. on Sc. (12).
- Schidrowitz, P. (6) p. 166. If time and temp. are constant Sc is dependent on the total amount of S in the mix.
- Schidrowitz, P. & Goldsbrough, H. A. (5) No proof that Sc at correct cure is a constant. (7) Stress-strain curve is a better method of judging cure than Sc. (9) The R. stress-strain curve.
- Seidl, E. (1) Effect of resins on Sc. (4) Vulc. and depolymerization.
- Skellon, H. (1) Sc is proportional to the concentration of S. Removal of resins lowers Sc.
- Spence, D. (19) Extraction curves for free S and for Sc. (21) Effect of temp. on Sc. At some temp. between 60-80° C. the velocity of vulc. suddenly increases. (22) No appreciable increase in Sc. at ordinary temp. (25) Sc at optimum cure is constant for Hevea R. at 2.8-3.0%. Balata needs at least 3% Sc.
- Spence, D. & Ward, C. A. (1) Effect of mastication on Sc.
- Spence, D. & Young, J. (1) Theory of vulc. Data on Sc. (2) Rate of increase of Sc at 50° to 75° C. Rate at 135° C. for R., gutta percha and balata.
- Stevens, H. P. (3) Effect of PbO on Sc. (6) Maximum Sc for properly cured R. not over 3.5%. (12) Crit-

- icism of stress-strain curves for judging cure. Sc is the best guide for a stable product. (17) Methods for determining state of cure. (18) Sc above 3.2% shows rapid deterioration. (22) The nature of vulc. (32) Change of Sc on ageing. (70) Excess of alum in coagulation retards vulc. and lowers Sc. (73) Correlation of physical properties and the chemical composition of R.
- Twiss, D. F. (4) Physical vs. chemical theories for combined S, Bibliography.
- Twiss, D. F. & Brazier, S. A. (1) The temp. coefficient for S between 128° C. and 168° C. is 2.5 for each 10° C. whether accels. are used or not. The Sc curve is rectilinear until the free S is almost completely exhausted.
- Unger, B. (1) During vulc. the R. reacts with not over 2% of S. (1885).
- deVries, O. (3) Rate of cure at 148° C. is double that at 140° C. (12) Pale crepe-100, S-7.5. Cure at 148° C. Natural ageing for 171 days or heating at 75° C. for 42 hrs. gives no change in Sc. Heating at 80° C. gives a slow increase. In all cases the stress-strain curve is lowered. Stress-strain data are preferable to Sc for judging cures. (14) No appreciable increase in Sc on storage of vulc. R. at tropical temps. The stress-strain curve moves downward as in continued curing. (15) Relation of Sc to degree of vulc. (20) Sc slowly increased during ageing below 90° C. (25) Relation of Sc to mechanical properties. Effect of natural vs. added accels.
- deVries, O. & Hellendoorn, H. J. (7) Effect of excess S on reversion of the stress-strain curve.
- Weber, C. O. (12) Brande in 1852 believed that not over 2% S combined with the R. (13) R-100, S-10. Sc curves for various times and temps. Vulc. is an additive process. No  $H_2S$  is formed (45) Effect of time, temp. and amount of S. (47) Resins are not converted into acetone insoluble compounds during vulc. The acetone extract is always higher after vulc. Sc should be calculated as per cent of S on pure R. Definition of Sc.
- Weil, R. (1) See Colloid Chemistry of Rubber.
- Wroblewski, V. (1) Sc is a linear function of temp.
- Sulfur Chloride.**
- Abbott, W. (1) Vulc. by  $S_2Cl_2$  vapors in 1878.
- Anon. (113) Solvents for  $S_2Cl_2$ . (115) Theory of cold vulc. (146) Dark colored  $S_2Cl_2$  is injurious to R. 15%  $S_2Cl_2$  on R. gives a horn like product. (232) & (243) Vapor cures followed by  $NH_3$  gas to neutralize free acid. (238) Old solutions of  $S_2Cl_2$  decompose and give a vulc. R. which ages poorly.
- Ayling, H. A. (1) Vulc. of R. by  $S_2Cl_2$  in light petroleum.
- Bamber, M. K. (1) Vulc. of latex by  $S_2Cl_2$ .
- Bernstein, G. (2) Nature of the action of  $S_2Cl_2$  on R.
- Birchall, F. W. (1) Poisoning by  $S_2Cl_2$ .
- Blanc, M. le & Kröger, M. (1) Organic accels. aid vulc. by  $S_2Cl_2$ .
- Bruni, G. & Amadori, M. (1) Solubility of S in  $S_2Cl_2$ .
- Bysow, B. V. (1) With solutions of low concentration, the combined S after 30 min. exposure, is proportional to the concentration. (2) The drier the R. the higher the combined S.
- Camille, A. (13) Methyl iodide accelerates cold vulc. giving efficiency and uniformity. (20) See Iodine. (21) 10%  $S_2Cl_2$  on R. gives a product which is not plastic at 312° F.
- Caspari, W. A. (1) Acts on gutta percha the same as on R.
- Claubry, H. G. de. (1) Chloride of lime is compounded into R. with S to produce  $S_2Cl_2$  "in situ" on heating.
- Dingler. (1) Résumé of work prior to 1873 by Payen, Fawsitt, Thorpe, Dalziel, Abbott, etc.
- Ditmar, R. (19) p. 87. List of 41 patents on the use of  $S_2Cl_2$  in R.
- Editorial. (2) Theories of Weber, Fawsitt, Burghardt, Thomson, Hörn & Minder on the action of  $S_2Cl_2$ .
- Esch, W. (8) Purify  $S_2Cl_2$  by blowing  $CO_2$  through it. The vulc. coefficient with  $S_2Cl_2$  is 1.6% S and 1.77% Cl on 100 parts R. This is lower than Weber's formula calls for.
- Fawsitt, C. A. (1.) (2) Properties, uses and analysis. Sulfur dichloride

- causes darkening and hardening of the R.
- Frank, F. & Marekwal, E. (7) Testing for purity.
- Gegenheimer, R. E. & Mauran, M. (1) Manufacture.
- Gottlob, K. O. (6) p. 97.
- Henriques, R. (2) The reaction of R. with  $S_2Cl_2$  is additive.
- Höhn, J. B. (1) Theories of vulc.
- Hinrichsen, F. W. (6) Effect of moisture on combined S.
- Hinrichsen, F. W. & Kindscher, E. (1) Cold Vulc. is a chemical process. (6) End products of the reaction of  $S_2Cl_2$  on R. (8) Theories.
- Hinrichsen, F. W. & Meisenberg, K. (1) Chemistry of cold vulc.  $S_2Cl_2$  on R. forms  $(C_{10}H_8)_2S_2Cl_2$ .
- Kindscher, E. (1) Historical review of theory and practice.
- Kirchhof, F. (2) Quantitative data on the addition of  $S_2Cl_2$  to R. Theory. Effect on viscosity.
- Klein, C. A. (1) Hygiene in the R. industry.
- Lascelles-Scott, W. (4) Ethyl iodide is an accel. of the cold vulc. process.
- Marekwal, E. & Frank, F. (8) MgO in R. vulc. with  $S_2Cl_2$  forms  $MgCl_2$  and  $MgSO_4$ . The S in  $S_2Cl_2$  takes no part in the vulc. process since it blooms out on the surface of the goods.
- Marzahn, R. (1) p. 119. Dark colored  $S_2Cl_2$  contains  $SCl_2$  which makes the R. brittle.
- Meyer, L. O. P. (5) Polemical with Thomson, W. (5).
- Minder, J. (1) Graphs showing effect of concentration in  $CS_2$  vs. time. 1899. (3) Decay of cold vulc. R. (4) Polemical with Höhn (1).
- Mueller, E. J. (1) Theories of cold vulc.
- Murrill, P. I. (1) Purification of  $S_2Cl_2$  by metallic Na. (3)  $S_2Cl_2$  should be dissolved in gasoline free from olefines.
- Ostwald, Wo. (1.)
- Ostwald, Wo. (1.) (2) Cold vulc. and the adsorption theory.
- Parkes, A. (1) First patent on vulc. by  $S_2Cl_2$ .
- Pearson, H. C. (1) p. 65.
- Porritt, B. D. (2) Notes on materials used in the R. industry.
- Potts, H. E. (1) (3) Polemical with Bysow.
- Robine, R. (1) Vulc. by mixed gases.  $S_2Cl_2$ , nitric acid and nitrous oxide.
- Schidrowitz, P. (6) p. 173. Review.
- Sheppard, S. R. (1) Use of  $S_2Cl_2$  in non-inflammable solvents.
- Stevens, H. P. (45) Spreading of vulcanized gels on fabric. (73) Alternative methods of vulc.
- Terry, H. L. (3)  $S_2Cl_2$  does not affect the health of workers. (6) The action of metallic halides in a R-S mix is to form  $S_2Cl_2$  "in situ."
- Thomson, W. (1)  $S_2Cl_2$  vulcanized R. by Cl and not by S. (4) All the chlorine in  $(C_{10}H_8)_2S_2Cl_2$  may be extracted by hot  $C_2H_5OK$ . (5) More Cl than S is combined with the R.
- Thomson, W. & Lewis, F. (1) See Arsenic Iodide. Test for differentiating between hot and cold cure on R. goods.
- Weber, C. O. (2)  $S_2Cl_2$  polymerizes R. by S linkages. Reaction with other unsaturated compounds. (4) Action of the chloride, bromide and iodide of S on R. (6)  $NH_3$  destroys HCl but not the odor in cold cured goods. (8) Polemical with Höhn (1). (38) See Ultramarine Blue. (40) Applications of cold cure. (61) p. 179. Composition, analysis and use.
- Weil, R. (1) See Colloid Chemistry of Rubber.
- Whittlesey, T. T. (2) Use of aniline to neutralize acid in cold cured goods
- Sulfur Dioxide.** See Enzymes, Latex-Coagulants, Latex-Preservatives and Peachey Process.
- Blossom, T. M. (1) No action on R.
- Byrne, F. A. (1) Action on R.
- Camille, A. (5)  $H_2SO_4$  has no harmful effect on R.
- Dubose, A. (23) See Vulcanization.
- Dubose, A. & Luttringer, A. (1) p. 181. R. and isoprene absorb  $SO_2$ .
- Fendler, G. (2)  $SO_2$  will gel a benzene solution of R.
- Fölsing. (1) Bleaching R. in solution.
- Goodyear, Chas. (4) Vol. 1, p. 155. Vulc. of R. by sulfurous gases in a heater.
- Ilken, C. A. & Down, St. V. B. (1) R. purified by soaking in a solution

of a salt (bisulfites, hyposulfites and sulfites) which will liberate  $\text{SO}_2$  when acidified.

Matthews, F. E. & Strange, E. H. (1) Natural or synth. R. treated with liquid  $\text{SO}_2$ . Product is then vulc. depending on the "vulcanization" already effected by the  $\text{SO}_2$ .

Parkes, A. (1) (2) Vapor cures with  $\text{SO}_2$ .

Reychler, A. (2) Absorption of  $\text{SO}_2$  by R. is only a solution phenomenon. (3) See Colloid Chemistry of Rubber.

Rossem, A. van. (6) Suggests treatment of R. after vulc. with  $\text{SO}_2$  on the basis that it is acidic and a negative accel.

Sisteron, X. F. (1) Bleaching R.

Traun, H. O. (1)  $\text{SO}_2$  passed into a  $\text{CS}_2$  solution of R. gives a white inelastic compound.

#### Sulfuric Acid.

Anon. (241) Acts harmfully on R. goods.

Achard, F. (1)  $\text{H}_2\text{SO}_4$  heated with R. forms a turpentine like mass from which water separates a black brittle resin.

Berghaus, H. (1) Conc.  $\text{H}_2\text{SO}_4$  chars balata, evolving  $\text{SO}_2$ .

Bing, K. (1) Old samples of vulc. R. show a water extract containing  $\text{H}_2\text{SO}_4$ . See Ageing-Tackiness.

Camille, A. (5) Action on R.

Eaton, B. J. (9) Retards vulc. of R. (26)  $\text{H}_2\text{SO}_4$  has a deleterious effect on raw R.

Fourcroy, A. F. & Nicholson, W. (1).

Gottlob, K. O. (6) p. 11. Conc.  $\text{H}_2\text{SO}_4$  has a charring effect on R.

Harries, C. (17) Action of conc.  $\text{H}_2\text{SO}_4$  on raw R. Kirchhof says this is the first real investigation on this subject.

Hatchett, C. (1) Caoutchouc was only superficially attacked by  $\text{H}_2\text{SO}_4$  on long digestion.

Heinzerling, C. (1) p. 29. Conc.  $\text{H}_2\text{SO}_4$  attacks crude R. vigorously leaving a black charry mass.  $\text{SO}_2$  is evolved. A mixture of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  attacks R.

Kirchhof, F. (6)  $\text{H}_2\text{SO}_4$  on R. in  $\text{C}_6\text{H}_6$  gives off  $\text{SO}_2$ . Product swells in R. solvents. Blackens at  $180^\circ \text{C}$ . with partial fusion. Br gives  $\text{C}_{10}\text{H}_{10}\text{OBr}_2$ .

See Oxygen. Some hydrogen in R. is oxidized by  $\text{H}_2\text{SO}_4$  as shown by the liberation of  $\text{SO}_2$ . Aldehyde acids are also formed. Constitution of R. molecule. Open chain vs. closed chain. (11) See Rubber-Structure and Chemistry.

Koller, P. (1) Action of conc.  $\text{H}_2\text{SO}_4$  on R. (1889).

Leonhardi, J. G. (1)  $\text{H}_2\text{SO}_4$  changes R. to a tough, brittle, non-elastic substance (1781).

Marquis, R. & Heim, F. (2) Action of  $\text{H}_2\text{SO}_4$  on R. in  $\text{CHCl}_3$  solution produces a white amorphous powder,  $(\text{C}_{10}\text{H}_{10})_{10}\text{H}_2\text{O}$ .

Martin, W. G. (1)  $1/8$  to 5%  $\text{H}_2\text{SO}_4$  added to R. on the mill retards vulc.

Mathews, R. (1) Aqueous  $\text{H}_2\text{SO}_4$  carbonizes R. when heated.  $\text{H}_2\text{SO}_4$  is formed (1805).

Morisse, L. P. T. (2) Vulc. with  $\text{H}_2\text{SO}_4$ . See Latex-Uses for.

Newbrough, J. B. (2)  $\text{H}_2\text{SO}_4$  and turpentine are heated together. The product is heated with R. to produce an ebonite. No S is used.

Nicholson, W. (1)  $\text{H}_2\text{SO}_4$  on R. evolves  $\text{H}_2\text{SO}_3$  (1808).

Obach, E. F. A. (1) Dil.  $\text{H}_2\text{SO}_4$  (1:20) does not attack gutta percha. Conc.  $\text{H}_2\text{SO}_4$  chars it.

Ramsay, Chick & Collingridge. (1) Action on gutta percha.

Reynaud, G. (4) A product of R., oil of turpentine and  $\text{H}_2\text{SO}_4$  having the physical properties of R.

Roxburgh, W. (1)  $\text{H}_2\text{SO}_4$  converts thin pieces of caoutchouc into black friable substance without dissolving it. Schidrowitz, P. (6) p. 216. Strong  $\text{H}_2\text{SO}_4$  chars soft R.

Seeligmann, Torrilhon & Falconnet. (1) p. 132. Same as C. Heinzerling (1).

Stevens, H. P. (28) Action of dil.  $\text{H}_2\text{SO}_4$  on Funtumia R. (30) Soaking R. in  $\text{H}_2\text{SO}_4$  strongly retards the cure.  $\text{HCl}$  less so, and acetic acid has little effect.

Thenard, L. J. (1).

Thomson, W. & Lewis, F. (1) See Hydrochloric Acid.

Whitby, G. S. (1) Describes a sample of R. left in 25%  $\text{H}_2\text{SO}_4$  for 18 months without becoming tacky.

Wiesner, J. (1) See Balata.

Wright, A. W. (1) See Ozone.

**Sulfur Iodide.**

- Fawsitt, C. A. (4) See Mercury Halides.  
 Terry, H. L. (6) p. 337. Will vulc. R. in a short time at ordinary temp.  
 Weber, C. O. (4) Same as Terry (6).

**Sulfur Oxychloride.**

- Peachey, S. J. (6) Used to halogenate R.

**Sulfur Reaction Products of Accelerators.**

- Bedford, C. W. (1) S reaction products of organic nitrogen compounds as accels. Mentions the S reaction products of thiocarbanilide, methylene aniline, methylene diphenyldiamine, p-phenylenediamine, triphenylguanidine, p-nitrosodimethylaniline, proteins, glue, etc.  
 Bedford, C. W. & Sebrell, L. B. (2).  
 Bruni, G. (1) Thiocarbanilide, phenyl mustard oil, phenylthiourea, methylene aniline, etc. react with S to produce mercapto benzothiazol.  
 Cadwell, S. M. (3) Aldehyde condensation products with amines are heated with S at 140° C. and the reaction product compounded into R. as an accel.  
 Hutin, A. (1) See Shellac.  
 Peachey, S. J. (9) p-Nitrosodimethylaniline heated with S at 135° C. Distillate and residue used as accels.  
 Pratt, W. B. (1) U. S. P., p. 2, lines 91-99. Depolymerized R. heated with S gives a product similar to the S reaction product of terpenes.  
 Rosenbaum, J. L. (1).  
 Wilhöft, F. (1) S reaction product of resins and balsams. See Sulfur-Bloom.

**Sulfuryl Chloride.**

- Anon. (130) Facilitates the action of Br on R.  
 Peachey, S. J. (13) Reaction with R.

**"Suparac Accelerators."**

- Anon. (48) Piperidine-pentamethylene-dithiocarbamate mixed with clay.  
 Schidrowitz, P. (43).

**"Super Sulfur."**

- Davies, E. L. (2) Recommended for use in R. mixes containing clay.

**Syneresis.**

- Blanc, M. le & Kröger, M. (1) Syneresis of R. gels vulc. with  $S_2Cl_2$ . Effect of org. accels.  
 Weil, R. (1) See Colloid Chemistry of Rubber.

**Tannin.****Tannic Acid.**

- Arisz, W. H. & van Schweizer, L. R. E. S. (1) Tannin in the R. tree.  
 Bayer & Co. (11) (16) (30) See Ageing-Oxidation.  
 Eaton, B. J. (16) Soaking fresh coagulum in dilute  $NH_4OH$ ,  $H_2BO_3$ , and tannic acid retards the rate of cure, while  $K_2CO_3$  and NaOH accelerate the cure. (17) Tannin retards vulc. (23) Tannin, boric, molybdic and phosphotungstic acids, which precipitate proteins, amines and basic nitrogenous materials, retard vulc. in slab and crepe R.  
 Fickenday, E. (1) See Ageing-Oxidation.  
 Fonrobert, E. & Harries, C. (1) See Ageing-Oxidation.  
 Heilbronner, A. (1) PbO replaced by reducing agents to obtain colored goods. Hydroquinone, pyrogallol, tannins, p-aminophenol, glycine, trioxymethylene and other HCHO derivatives, hydrosulfites, neutral sulfites, etc. Not over 10% should be used.  
 Ostromuilenskii, I. (13) See Ageing-Oxidation.  
 Pearson, H. C. (1) p. 166. Injurious to R.  
 Schulte, A. (1) See Latex-Coagulation.  
 Zingler, M. (1) (2) See Ageing-Tackiness.

**Tar.**

- Frank, F. & Marckwald, E. (9) Properties of coal tar solvents.  
 Peter, L. (1) "Middle tar oil" as an "elasticator."  
 Weber, C. O. (53) Use of hard pitch in R. goods.

**Tartar Emetic.**

- Zingler, M. (1) (2) See Ageing-Oxidation.

**Tartaric Acid.**

- Eaton, B. J. (17) A good latex coagulant. Gives same results as acetic acid.



Morgan, S. (1) p. 216, 227. Retards vulc. when used as a coagulant.

### **Tellurium.**

Fahrenwald, F. A. (1) Vulc. R. reclaimed by heating with Te.

Gottlob, K. O. (6) p. 97. Possesses vulcanizing properties.

Klopstock, H. (1) Vulc. with Te Chloride. See Selenium.

Smith, H. E. (1) R. vulc. with Te or Se resists heat and oxidation better than when cured with S. Te used in air-bags, hot water bottles, inner tubes, etc. Vulc. at 350° F. to 400° F.

### **Terpineol.**

Beyer, C. (1) Preserves the elastic properties of vulc. R.

Ostromuiskii, I. (13) A weak accel. when used with metallic oxides. See Xanthates. (22) See Colophony.

### **Tertiary Amines.**

Ostromuiskii, I. (13) See Amines.

### **Tetrabromide of Rubber.** See Bromine and Chlorine.

Axelrod, S. (4) The tetrabromide of vulc. R. is different from the tetrabromide of raw R.

Becker, R. (1) R. resins give insoluble bromination products. R. should be freed from resins prior to preparing the tetrabromide. (2) Prolonged contact of rubber tetrabromide with warm bromine gives a product which is insoluble in  $\text{CHCl}_3$ . This may be a higher brominated product.

Budde, T. (1) Rubber resins and oxidized R. do not react with bromine. (3) R. determined as the tetrabromide in goods vulc. with  $\text{S}_2\text{Cl}_2$  in absence of heavy metals. Resins, oils and substitutes yield no insoluble bromination products. (5) Low results obtained with the tetrabromide determination of R. as compared with the nitrosite method are due to presence of R. resins. (6) Analysis of cold vulc. R. (7) Bromine on vulc. R. oxidizes free S but does not affect combined S. (8) Influence of moisture and proteins on determining R. as the tetrabromide.

Dubosc, A. & Luttringer, A. (1) p. 168. Bromide of R. when heated at 30

to 60° C. splits off HBr. Decomposition is not complete at 150° C. Alcoholic soda does not attack the tetrabromide. Partially attacked by sodium ethylate under pressure at 100° C. Indifferent to mineral acids. Fuming  $\text{H}_3\text{PO}_4$  slowly attacks it. Boiling chromic acid or chromic-sulphuric acid mixture do not attack it.

Esch, W. (12) Determination of vulc. R. as tetrabromide gives widely varying results. The combined S which is oxidized by atmospheric oxygen under ordinary conditions, is also affected by the action of bromine.

Harries, C. (31) p. 12.

Harries, C. & Rimpel, H. (1) Comparison of bromide and nitrosite methods of analysis of raw R.

Hinrichsen, F. W. (8) Tetrabromide with alcoholic NaOH gives a bromine free product. The action of halogens on R. is affected by light. NaOH removes HCl from R. cured with  $\text{S}_2\text{Cl}_2$ .

Hinrichsen, F. W. & Manasse, W. (1) Objections to the Axelrod method of analysis by the tetrabromide method.

Hinrichsen, F. W., Quensell, H. & Kindscher, E. (1) Brominating an ice cold solution of R. gives the tetrabromide irrespective of the amount of bromine used or duration of the action.

Hübener, G. (1) Analysis of ebonite. (3) Analysis of vulc. R. (4) Tetrabromide method of analysis of R. (5) Reply to Becker (1) & (2). (6) Asphalts and bitumens cause errors in tetrabromide analyses. (7) Influence of resins in the bromination of R.

Kindscher, E. (11) Tetrabromide determination of R.

Kirchhof, F. (3) One-half of the combined bromine is removed by alcoholic KOH at 100° C., the remainder at higher temp. Bromine free product is isomeric but not identical with normal caoutchouc. Metallic calcium and the tetrabromide give an elastic product, while aniline gives an elastic product.

Korneck, O. (2) Errors in tetrabromide analysis.

- Spence, D. (17) Action of bromine on proteins.
- Spence, D., Galletly, J. C. & Scott, J. H. (1)  $\text{HNO}_3$  attacks the tetrabromide with a loss of bromine, even in presence of  $\text{AgNO}_3$ . Proteins are precipitated by bromine along with the tetrabromide.
- Tetraethylthiuramdisulfide.** See Tetramethylthiuramdisulfide.
- Tetralin.**
- Tetrahydronaphthalene.** b.p. 205-207° C.
- Ditmar, R. (64) A retarder in the preparation of facts.
- Utz, K. (5) Chemical and physical properties. A good R. solvent.
- Tetrahydropyrrrol.** See Pyrrolidine.
- Tetramethyl-diamido-diphenyl-thiourea.**
- Bedford, C. W. & Sibley, R. L. (3) By action of  $\text{H}_2\text{S}$  on p-Nitrosodimethylaniline in  $\text{CS}_2$ .
- Kratz, G. D., Flower, A. H. & Coolidge, C. (1) Relative curing power of several accels.
- Spence, D. (28) More active an accel. than thiocarbaniide.
- Tetramethylenediamine.** Putrescene.
- Anon. (84).
- Bayer & Co. (6) Derivatives as accels. (13) Used in synth. R. (14) An accel. for soft R. or ebonite.
- Ditmar, R. (62).
- Eaton, B. J. (8). (21).
- Gottlob, K. O. (7).
- King, A. H. (1).
- Pearson, H. C. (1) p. 84.
- Simmons, H. E. (1).
- Whitby, G. S. (8) p. 190.
- Tetramethylether of the Tetrahydrophenol Derivative of Rubber.**
- Fisher, H. L. & Gray, H. (1). Preparation.
- Tetramethylthiourea.**
- Bayer & Co. (14) An accel.
- Maximoff, A. (1) Not an accel.
- Tetramethylthiuramdisulfide.**
- Bedford, C. W. & Sebrell, L. B. (1) (2) Chemical reactions and mechanism of action as a curing agent and as an accel.
- Bruni, G. (1) R-100, ZnO-5, Thiuram-0.5. Cure 15 min./145° C.
- Bruni, G. & Romani, E. (1) Curing reactions of mono- and disulfides.
- Cadwell, S. M. (1) (2) See Xanthates.
- (5) (6) Thiuram monosulfides. (7) Mentions several substituted thiurams as accels.
- Geer, W. C. (1).
- Lorentz, B. E. (1) Patent.
- Maximoff, A. (1) The disulfide loses one atom of S to the R. and changes to the monosulfide. The monosulfide is comparable with the disulfide as an accel.
- Molony, S. B. (1) See Dithiocarbamates.
- Murrill, P. I. (5).
- Romani, E. (1) Manufacture. Vulc. of R. without free S. ZnO increases its activity as an accel. See Pentamethylenethiuramdisulfide.
- Schidrowitz, P., Gouvea, J. M. S. & Osborne, F. G. (1) See Dimethylammonium-dimethyldithiocarbamate.
- Twiss, D. F. (12) Mentioned in footnote. (14) Thiuram disulfides derived from primary amines are weaker than those from secondary amines. Mentions tetraethylthiuramdisulfide.
- Twiss, D. F., Brazier, S. A. & Thomas, F. (1) Almost inactive as an accel. in the absence of ZnO. The tetraethyl thiuram is more active than the tetramethyl derivative.
- Tetramethylurea.**
- Bayer & Co. (14) An accel.
- Tetranitromethane.**
- Ostromuiskenskii, I. (15) Will not vulc. R. under any condition.
- Tetranitronaphthalene.**
- Ostromuiskenskii, I. (25) Will vulc. R. in absence of S. See Dinitrobenzene.
- Tetranitrophenolphthalein.** See Aurotin.
- Tetraoxyphenyl Derivative of Rubber.**
- Ditmar, R. (47) p. 42.
- Dubosc, A. & Luttringer, A. (1) p. 200.  $\text{C}_{10}\text{H}_{10}\text{Br}_4 + 4\text{C}_6\text{H}_5\text{OH} = \text{C}_{10}\text{H}_{10}(\text{O}-\text{C}_6\text{H}_5)_4 + 4\text{HBr}$ .
- Gottlob, K. O. (6) p. 5.
- Weber, C. O. (14) Cresols, carvacrol, thymol, naphthol, resorcinol, pyro-

catechol, hydroquinone and phenol react with R. tetrabromide to give this type of compounds.

**Tetraoxyphenyl-dioxyrubber.**  $C_{10}H_{10}O_2$   
( $O-C_6H_5$ )<sub>4</sub>.

Ditmar, R. (47) p. 42.

Gottlob, K. O. (6) p. 5.

Hinrichsen, F. W. & Memmler, K. (1) p. 51.

Weber, C. O. (14) Prepared from R. tetrabromide and phenol.

**Theories of Vulcanization.** See Vulcanization-Theories.

**Thioacetyl disulfide.**

Cadwell, S. M. (5) (6) An accel.

**Thioacids.** See Dithioacids.

**Thioamides.**

Cadwell, S. M. (5) (6) See Xanthates.

**Thioaniline.**

Kimishima, T. (1) Thio- and dithioaniline have little accelerating action on R & S when vulc. in hot air. In an atmosphere of  $H_2S$ , dithioaniline is very active. The R. mix may be saturated with  $H_2S$  in the cold and later vulc. in a press. No  $ZnO$  was used in these tests.

**Thiobenzamide.**

Cadwell, S. M. (5) An accel.

**Thiobenzanilide.**

Cadwell, S. M. (5) (6) An accel.

**Thiobenzoic Acid Anhydride.**

Cadwell, S. M. (7) An accel.

**Thiobenzoyl disulfide.**

Cadwell, S. M. (5) (6) An accel.

**Thio-camphor.** (Thio-campf).

Parkes, A. (1) A solvent for R. prepared by passing  $SO_2$  into camphor.

**Thiocarbamates.** See Dithiocarbamates.

Cadwell, S. M. (5) (6).

**Thiocarbamilide.** Diphenyl-thiourea.  
(T.C.A.)

Anon. (300) Ineffective in the absence of basic fillers.

Bedford, C. W. (1) S reaction product of T.C.A. as an accel. See Mercaptobenzothiazole. (2).

Bedford, C. W. & Scott, W. (1)

T.C.A. will not vulc. R. in absence of free S. See Dubosc, A. (40).

Bedford, C. W. & Sebrell, L. B. (1) T.C.A. forms a Zn salt through its mercapto form which with S will vulc. R. at ordinary temp. (2) Lead salt of T.C.A.

Bedford, C. W. & Sibley, R. L. (1) p-Nitrosodimethylaniline used as a catalyst in the preparation of T.C.A. Bruni, G. (3) See Dithiocarbamates. Dannerth, F. (1).

Davies, E. L. (2) Does not work well with clay.

Dubosc, A. (40) T.C.A. can furnish all the S necessary for vulc.

Earle, D. (1) T.C.A. is probably the least poisonous of all accels.

Endres, H. A. (1) Comparison of several accels.

Fry, H. S. (1) Methods of preparation.

Geer, W. C. (2) First used as an accel. at the Diamond R. Co. in 1907.

Kelly, W. J. & Smith, C. H. (1) Manufacture.

King, A. H. (1) Alkali sulfides as catalysts in the preparation of T.C.A.

Kratz, G. D., Flower, A. H. & Coolidge, C. (1) T.C.A. functions as an accel. by decomposition into aniline. Comparison of the curing power of phenylmustard oil, T.C.A., aniline and triphenylguanidine.

Kratz, G. D., Flower, A. H. & Shapirc, B. J. (2) T.C.A. is not entirely inactive in absence of  $ZnO$ . More active than aniline when  $ZnO$  is present. See Aniline.

Murrill, P. I. (5).

Pickles, S. S. (1).

Price, R. B. (1) Fabric is impregnated with T.C.A., lime, lead resinate,  $Na_2S$ , K stearate, etc., to give a better union to R.

Rubber Service Laboratories Co. (1) Scorching in a T.C.A. mix is prevented by replacing a part of the T.C.A. with methyleneaniline.

Schidrowitz, P. (13) Curing data. (15) 1%  $ZnO$  used to activate T.C.A.

Scott, W. & Bedford, C. W. (1)  $H_2S$  reacts on T.C.A. to give the aniline salt of phenyldithiocarbamic acid.

Shepard, N. A. & Krall, S. (2) See Hexa.

Simmons, H. E. (1).

- Spence, D. (28) T.C.A. is not as powerful as its tetramethyldiamido derivative.
- Twiss, D. F. (9) Effect of ZnO.
- Twiss, D. F. & Brazier, S. A. (1) Curing data on T.C.A. with ZnO.
- Twiss, D. F., Brazier, S. A. & Thomas, F. (1) Effect of ZnO.
- Twiss, D. F. & Howson, C. W. H. (1) See Carbodiphenyldiimide.
- Venable, C. S. & Fuwa, T. (1) Permeability and solubility of gases in R. cured by the aid of T.C.A.
- Venable, C. S. & Green, C. D. (1) Solubility of S in R. cured by the aid of T.C.A.
- Weber, L. E. (9) 2-4% used for each 100 parts of R. Tends to scorch on mills and calenders.
- Whitby, G. S. & Walker, O. J. (1) T.C.A. is without accelerating effect in R-90, S-10.
- Thiocarbonates.** See Trithiocarbonates.
- Fawsitt, C. A. (4) R. is cured by heating with a mixture of metallic halides and trithiocarbonates.
- Thiocarbo-p-toluidide:**
- Di-p-tolythiourea.**
- Twiss, D. F. (12) Curing data with and without ZnO.
- Thioflavine T.**
- Gaisman, L. & Rosenbaum, J. L. (1) An accel.
- Thioformanilide.**
- King, A. H. (1).
- Thiolcarbonates.**
- Cadwell, S. M. (5) (6) See Xanthates.
- Thionine Blue.** See Lauth's Violet.
- Gaisman, L. & Rosenbaum, J. L. (1) An accel.
- Thiophenol.**
- Bedford, C. W. & Sebrell, L. B. (1) Will vulc. a R-S-ZnO cement at ordinary temp.
- Thiophenylacetyldisulfide.**
- Cadwell, S. M. (5) (9) An accel.
- n-Thiopipecridine.**
- Bayer & Co. (5) (6) (9) (13) (14) An accel. R-100, S-10, Accel.-1.0. Cure 1 hr./125° C.
- Thioresorcinol.**
- Lascelles-Scott, W. (22) Philothion and thioresorcinol have practical value in the vulc. of fine rubbers.
- Thiosulfates.**
- Fawsitt, C. A. (4) R. vulc. by a mixture of metallic iodides and thiosulfates.
- Levinstein, E. (1) Metallic thiosulfates loose one atom of S and may be used, with or without S for the vulc. of R.
- Thiourea.**
- Dubosc, A. (40) An accel.
- Kratz, G. D., Flower, A. H. & Coolidge, C. (1) See Aniline.
- Thiuramdisulfides.**
- Thiuram-monosulfides.** See Tetramethylthiuramdisulfide.
- Thymol.**
- Ditmar, R. (10) See Latex-Preservatives.
- Tin.** See Metals.
- Weber, C. O. (9) Tin mordants have no effect on dry heat cured goods. Slight effect on cold cured goods.
- Tin Dithiocarbamates.**
- Molony, S. B. & Nikaido, Y. (1) (2).
- Tin Iodide (Bromide).** See Antimony Iodide.
- Fawsitt, C. A. (1) See Mercuric Iodide.
- Titanium Oxide.**
- Barton, L. E. (1) Gives increased resistance to tear and shortens the time of cure.
- Barton, L. E. & Gardner, H. A. (1) A white pigment which is a mild accel.
- Heaton, N. (1) A mixture of BaSO<sub>4</sub> and titanium oxide as a R. pigment.
- Tolueneazotoluene-beta-naphthol.**
- Dyer, J. W. W. (1) See Ageing.
- Tolidine.**
- Bayer & Co. (41) See Ageing-Tackiness.
- o-Toluidine.**
- Bedford, C. W. & Sebrell, L. B. (1) Zn dithiocarbamates of the toluidines.

- Cadwell, S. M. (3).  
 Duisberg, C. (1) Use in synth. R.  
 Endres, H. A. (1) Comparison of several accels.  
 Gottlob, K. O. (8) Imparts elasticity to synth. R.  
 Hasselt, J. F. B. van. (1) See p-Nitrosodimethylaniline.  
 Hodgson, H. (1) Reaction product of S and o-toluidine.  
 Twiss, D. F. (6) Na or K hydroxides in o-toluidine as accels. (12) Mentioned.
- m-Toluidine.**  
 Bedford, C. W. & Sebrell, L. B. (1) See o-Toluidine.  
 Twiss, D. F. (6) See o-Toluidine.
- p-Toluidine.**  
 Bayer & Co. (32) Toluidine sulfate as an accel.  
 Bedford, C. W. & Sebrell, L. B. (1) See o-Toluidine.  
 Cadwell, S. M. (1) (2) (3) (5) (6).  
 Dubosc, A. (42). (48) S reaction products.  
 Endres, H. A. (1) Comparison of several accels.  
 Gaisman, L. & Rosenbaum, J. L. (1).  
 Kratz, G. D., Flower, A. H. & Shapiro, B. J. (1) See Aniline.  
 Twiss, D. F. (12) Graphs for R-90, S-10, Accel.-1.0 with and without zinc oxide.
- Toluidine Trithioozonide.**  
 Ostromuiskenskii, I. (17).
- m-Toluylenediamine.** See Aldehyde-Amines.  
 Bedford, C. W. & Sebrell, L. B. (1) The amine, its disulfide or disulfide-polysulfide as accels.
- Triaminotoluol.** See Aldehyde-Amines.
- Trichloroacetic Acid.**  
 Davidson, S. C. (3) See Latex-Coagulation.  
 Spence, D. & Kratz, G. D. (1) See Viscosity.
- Trichlorethylene.**  
 Anquetil, C. E. (1) Used to dissolve R. for purification.
- Trimethylamine.**  
 Dubosc, A. (40) An accel.
- Trimethyleneimine.**  
 Eaton, B. J. (8) An accel.
- Trimethylenetriamine.**  
 Anon. (84).  
 Dubosc, A. (40) An accel.  
 King, A. H. (1).
- Trimethylenetrianiiline.** See Methylene-aniline.  
 Murrill, P. I. (5) An accel.
- Trinitroamino Cobalt.**  
 Dubosc, A. (15) An accel.
- Trinitroaniline.**  
 Ostromuiskenskii, I. (17) Not an accel.
- Trinitrobenzene.** (TNB).  
 Buntschoten, E. (1) Review of the work of Ostromuiskenskii.  
 Ostromuiskenskii, I. (14) Vulc. at ordinary temp. with TNB & PbO. (19) As little as 0.5% of TNB will vulc. R. (25). (30) R-10, S-1, PbO-3, TNB-1. Cure 30 min./142° C. Non-blooming. High tensile. (31).  
 Porritt, B. D. (2) Inactive in the absence of oxides.  
 Stevens, H. P. (10) Review. (45) Vulc. of R. cements by TNB in the presence of MgO, PbO or the litharge product of a fatty oil.  
 Sumitomo, K. (1) TNB used to vulc. insulation for copper wire without the use of S.
- Trinitrobutylxylene.** See Artificial Musk.
- Trinitronaphthalene.**  
 Ostromuiskenskii, I. (25) See Dinitrobenzene.
- Trinitrophenol.**  
 leRoy, G. A. (1) See Phosphorous Thiobromide.
- Trioxymethylene.**  
 Heilbronner, A. (1) See Tannin.
- Triphenylguanidine.** (TPG).  
 Bedford, C. W. (1) S reaction products as accels.  
 Bedford, C. W. & Sebrell, L. B. (2) Reactions of.  
 Blanc, M. le & Kröger, M. (1) See Viscosity.  
 Kratz, G. D., Flower, A. H. & Coolidge, C. (1) Reacts with H<sub>2</sub>S to form aniline and thiocarbanilide. **Has**

lower curing power than the mono- or diphenyl derivatives. See Aniline.  
Murrill, P. I. (5).  
Schidrowitz, P. (19).  
Twiss, D. F. & Howson, C. W. H. (1) Tensile and elongation curves for R-90, S-10, TPG-1, with and without ZnO.  
Weber, L. E. (9) TPG is less active than diphenylguanidine. 1.25% to 1.50% are safe amounts to use. Works well with antimony sulfide.

**Triphenylmethane.**

Ostromuiskii, I. (15) Will not vulc. R.

**Triphenylmethane Dyes.** See Dyes.

Meeus, E. de. (1) The dye bases are accels.

**Trithiocarbonates.**

Cadwell, S. M. (5) Mono-, di- and trithiocarbonates, their metallic salts, esters and derivatives as accels.

**Trithioozone.**

Bedford, C. W. & Sebrell, L. B. (2) Formed by the action of  $H_2S$  and  $SO_2$ . Will vulc. R. at ordinary temp.  
Ostromuiskii, I. (17) The action of amines is to produce trithioozone. Predicts the discovery of a trithioozone which will vulc. R. directly. See Amines, Vulcanization-Theories, Light.

**"Tuffine."**

Anon. (104) An accel.

**Tungsten Oxide.**

Newbrough, J. B. (1) See Iodine.

**Tyrosin.**

Eaton, B. J., Grantham, J. & Day, F. W. F. (1) A weak accel.

**Tyrosinase.**

Gorter, K. (12) The cause of discoloration of R.  
Jong, A. W. K. de. (3) Causes discoloration in R.

**Ultramarine Blue (UB).**

Breuil, P. (13) UB preserves R. against over vulcanization.  
Peachey, S. J. & Skipsey, A. (2) UB tends to prevent vulc. of R. by  $H_2S$  and  $SO_2$ .  
Weber, C. O. (38) UB is injurious in cold cured goods.  $AlCl_3$  is formed.

**Ultraviolet Light.** See Light.

**Uranium Borate.**

Anon. (82) Mixed with latex before coag. Increases tensile and prevents oxidation of the R.

**Uranium Oxide (black).**

Lascelles-Scott, W. (26)  $U_3O_8$  exerts a distinctly preservative influence on R.

**Uranium Sulfide (black).**

Lascelles-Scott, W. (26) Exerts a reducing and therefore preserving influence on R.

**Urea.**

Anon. (84) Urea derivatives as accels.  
Bayer & Co. (4) & (21) Urea, starch, albumen, blood serum and glycerine as polymerizing agents in synth. R.  
Cadwell, S. M. (3) See Aldehyde-Amines.  
Ditmar, R. (22) & (62) Mentioned.  
Eaton, B. J. (8) Urea derivatives as accels.  
King, A. H. (1).  
Kratz, G. D., Flower, A. H. & Coolidge, C. (1) Urea first discovered as an accel. from the fast curing of African R. said to have been coagulated with urine. Urea slightly more active than thiourea. See Aniline.  
Pearson, H. C. (1) See p. 87.  
Rowley, T. (1) Stale urine as a source of  $NH_3$  for acceleration.

**Valeraldehyde.** See Aldehyde-Amines.

**Valeraldehyde-aniline.**

**Valeraldehyde-monoethylamine.**

Cadwell, S. M. (3) See Aldehyde-Amines.

**Vanadium (Va).**

Anon. (122) Mixture of  $Cr_2O_3$  and a Va salt used in R. facilitates the formation of colloidal S.  
Dubosc, A. (40) Va salts shorten the time required for vulc. See Sulfur Dioxide.  
Lee, J. E. (1) Va toughens R., increases tensile, decreases porosity and makes R. water and oil proof.

**Variability of Crude Rubber.**

- Anon. (11) Chemical analysis gives no indication of variability of R. from trees of different age. (34) Editorial review on variability of plantation R. (38) Hand tests do not show the variability in smoked sheet. Causes and prevention of variability. (163) Variation caused by methods of coag. (205) Quick drying gives high quality R. (261) Smoking lengthens the time of cure. Drying methods have little effect. Moist R. increases in rate of cure. Thin crepe cures slowly. Blanket crepe cures same as smoked sheet. (266a) Smoking sheet R. 3, 7 or 14 days has no appreciable effect on time of cure or quality of the vulc. R. Smoked crepe, slightly longer time of cure than unsmoked crepe. The amount of rolling which crepe receives on plantations has no marked adverse effect on R. Spontaneously coagulated R. as a rule cures more rapidly than crepe R. coagulated with acetic acid. R. allowed to remain in a moist condition has a quick rate of cure and the presence of creosote does not prevent but may lessen the effect on time of vulc.  $K_2C_2O_4$  added to latex decreases time of cure without affecting tensile strength. Addition of  $CaCl_2$  to latex decreases the strength without affecting the time of cure. Addition of old latex serum to fresh latex reduces the time of cure without affecting the mechanical properties. NaOH added to latex before coagulating with acetic acid considerably increases the time of cure and reduces the tensile strength slightly. HCHO as a latex preservative increases the rate of cure considerably without affecting the mechanical properties; the minimum amount should be used. Acetic, formic, sulfuric and hydrofluoric acids all increase the time of cure when used in 4 to 8 times the minimum amount. Excess of acetic acid is less objectionable than the other three.  $H_2SO_4$  in excess has an adverse effect on the mechanical properties. (300) Polemic between H. P. Stevens and J. B. Tuttle on testing plantation R.
- Arens, P. (2) Preparation of uniform plantation R.
- Campbell, L. E. (1) Creping fresh coag. R. retards rate of vulc. Further working has no effect. No variation due to drying in hot air or vacuo.
- Cayla, V. (7) Variability influenced by treatment of R. before, during and after coag.
- Dunstan, W. R. (1) No difference in R. from young or old trees.
- Eaton, B. J. (10) Causes of variability in rate of cure. (13) The smoking of Para R. retards the rate of cure. (16) Drying slab R. at  $160^\circ$  F. retards rate of cure while drying at  $130^\circ$  F. accelerates the cure. Smoking, excessive creping or soaking in running water retards rate of vulc. (18) Variability caused by thickness of sheet, smoking, use of preservatives, amount of coagulant and dilution of latex. Due to different amounts or quality of non-caoutchouc constituents remaining in the R. (19) Slab R. is less variable due to less handling. 20% higher tensiles than crepe and superior to smoked sheet. (26) Variability in rate of cure due to varying amounts of natural accels. dependent on treatment. List of factors causing variability.
- Eaton, B. J. & Grantham, J. (3) Variability of plantation R. obscured by the use of org. accels. (4) Smoked sheet cures slower than unsmoked sheet. (5) Variability due to natural accels. present in latex, probably protein or a decomposition product of a protein.\* (6) Variation is chiefly related to rate of vulc. and is not indicated by the mechanical properties of the raw R. A rapid curing R. has superior keeping qualities.
- Eaton, B. J., Grantham, J. & Day, F. W. F. (1) Pale crepe more variable than Para R. Natural accels. probably amines or amino acids. Smoking, formalin, boric and tannic acids retard vulc. The lower the N content the faster the rate of cure. Mineral acids are injurious. Alum is objectionable.  $H_2SO_4$  is permissible. Litharge overrides variations in rate of cure.

- Gorter, K. (9) Data on variability from W. Java exp. Station (1915).
- Hartjens, J. C. (1) "Shortness" increased by  $\text{HCHO}$  and diminished by  $\text{NaHSO}_4$ . Methods of coag. have no effect.
- Kaye, F. (2) & (3) Variability from inequalities in latex and methods of coag.
- Morgan, S. (1) p. 142. Defects in crepe and block R.
- Pickles, S. S. (3) Rate of cure, effect of milling, over curing and ageing.
- Schidrowitz, P. (4) Pale crepes which contain the least free acid vary more in quality than smoked sheets which should contain more free acid than any other variety. (42) Effect of accels. on the variability of plantation R.
- Schidrowitz, P. & Goldsbrough, H. A. (2) Effect of amount of acetic acid in coag. Unsmoked plantation R. may be prepared equal to the best wild R. (8) Smoked sheet cures faster than crepe.
- Spoon, W. (6) Dilution of latex with sea water decreases tensile strength, rate of cure and viscosity of R. Greater effect on sheet than crepe R.
- Stevens, H. P. (9) The difference between smoked and unsmoked R. is greater than indicated by Whitby, G. S. (4). (19) Variation due to nature and amount of non-caoutchouc constituents of R. Removal of proteins and resins retards vulc. (27) Naturally coag. R. is more variable than crepe due to variable conditions of fermentation. (31) Para R. shows the same variation as plantation R. (37) See Slab Rubber. (44) Disinfection of tapping cuts has no effect on variability. (47) Use of  $\text{ZnO}$  in crude R. tests is undesirable. Pure Gum mixes are more suitable for testing variation. (49) Storage of plantation R. tends to develop uniformity. (50) Delay between coag. and rolling increases rate of cure. Serum left in sheet R. is a potential source of acceleration. Smoke is an antiseptic and retards the formation of accels. (51) A simple R-S mix is best for testing variability. (55) Variability tests on crude R. (56) See Slab Rubber. (60) Effect of surface slime on rate of vulc. (78) Ageing tests on plantation R. show absence of variability.
- Tuttle, J. B. (1) PbO and org. accels. cause much of the variability of plantation R. to disappear.
- Twiss, D. F. (9) Résumé on variability.
- deVries, O. (1) Review of Eaton's work on variability. (2) Relative value of crepe and smoked sheet. (4) Smoked sheet cures faster and is more variable than crepe. (6) Rate of vulc. decreases with the age of the tree. (10) Dilution of latex retards rate of cure. No effect on tensile, slope or viscosity. (23) Drastic tapping gives a R. with an increased rate of cure. Tapping early or late in the day has no influence. (26) Latex diluted with serum gives a faster curing R. but less uniform than when water is used. (27) Variation in plantation R. decreases on storage. Crepe R. increases in curing power without change in tensile. Matured R. is practically unchanged. (28) Factors promoting oxidation decrease the quality of the R. and vice versa. (29) Causes of variation.
- deVries, O. & Hellendoorn. (4) Fresh rolled crepe gives lower rate of cure and tensile strength when heated above  $40^\circ \text{C}$ . Fresh sheet dried at  $40-50^\circ \text{C}$ . gives same results as air dried but at  $60^\circ \text{C}$ . a decrease in rate of cure is noted. Rate of cure of dry R. unaffected by heating to  $70-100^\circ \text{C}$ . although tensile strength decreases.
- deVries, O. & Spoon, W. (2) Causes of variability.
- Weber, C. O. (42) Smoking Para R. and its effect. Smoking is not essential to good rubber. (46) Rate of cure of plantation R.
- Whitby, G. S. (3) Remarks on smoked R. (4) Only a slight increase in rate of vulc. from undiluted latex kept 5 hrs. before coag. (8) p. 178 & 184. Comparison of sheet and crepe R. The latter is slower curing. p. 201. Comparison of variation in para and plantation R.
- Wildman, E. de. (2) Avoid great dilution of latex, use minimum



amount of coagulant and smoke at not over 55° C.

Williams, W. A. (1) Para R. more uniform than plantation R.

#### **Vaseline.**

Ahrens, F. (5) See Ageing-Oxidation.  
Grossmann, P. (1) See Ageing-Oxidation.

Himmelbauer & Co. (1) See Ageing-Oxidation.

#### **Vermillion.**

Gottlob, K. (6) p. 69. Non-poisonous.

#### **Victoria Blue.**

#### **Victoria Green.**

Mecus, E. de. (1) See Dyes.

**Viscosity.** (V). See Colloid Chemistry of Rubber, Ageing-Oxidation, Ageing - Tackiness, Depolymerization, Light.

Anon. (284) Relation of V. to quality of R. (302) V. of R. colloids.

Ahrens, F. (1) Amyl acetate added to a 10% solution of R. reduces the V. so that it may be filtered thru filter paper. Effect of milling on V. Light causes oxidation and oxidation reduces V.

Axelrod, S. (3) V. of R. solutions. (5) V. as a measure of the quality of the R. and of depolymerization.

Barrowman, M. (1) V. of latex at different dilutions.

Beadle, C. & Stevens, H. P. (14) Effect of mechanical treatment and temp. of drying on V.

Bernstein, G. (2) V. of solutions of vulc. R. See Light. (3) Effect of heating and milling on V. (4) Effect of acids on V. (5) V. is lowered by mechanical treatment, heat and light. See Depolymerization.

Blanc, M. le & Kröger, M. (1) V. of R. solutions vulc. with and without accels. As vulc. (with S or S<sub>2</sub>Cl<sub>2</sub>) proceeds, the V. first drops and then increases. Effect of different solvents. Effect of the following accels. on the V. of R. solutions. p-Nitrosodimethylaniline, p-aminodimethylaniline, triphenylguanidine, piperidine, aldehyde ammonia, quinoline, betanaphthylamine, m-dinitrobenzene and brucine. Also iodine, benzyl alcohol, acetic and chloracetic acids.

Eaton, B. J. (2) Discussion of the work of J. G. Fol. (4) V. measurements.

Fol, J. G. (1) Effect of mastication. (2) V. is a direct indication of the quality of the R. Resins diminish V. (3) V. of a R. solution decreases with age. Filtering out the insol. matter lowers V. (7) High V. generally indicates good mechanical properties after vulc.

Frank, F. (11) V. determinations by International R. Testing Committee.

Frank, F. & Marckwald, E. (3) V. can only be used as an indicator of quality when comparing Rs. of the same class, prepared in the same manner.

Gaunt, R. (1) V. of R. in various solvents.

Gorter, K. (8) "Viscosity Index." Log of V. of a 1% solution of R. V. index times 70 = tensile strength.

Hatchek, E. (1) Theory of V. in 2 phase systems.

Heurn, F. C. van. (2) R. with low V. can be cured to equal properties with high V. R. by longer cures and without over curing.

Kawakami, K. (1) V. is not an absolute function of depolymerization.

Kirchhof, F. (2) Effect of Br, O<sub>2</sub> and S<sub>2</sub>Cl<sub>2</sub> on V. (5) Influence of solvents on V.

Munro, A. M. (1) No direct relation between V. and tensile strength. Effect of resins on the V. of R. in CHCl<sub>3</sub>.

Netherlands Government. (1) Determination of V. as relative viscosity. (6) Résumé of methods of expressing V. Determination of relative viscosity described.

Rossem, A. van. (2) Reduction of V. proceeds more rapidly in O<sub>2</sub> than in CO<sub>2</sub>. (3) V. of R. dissolved from latex vs. V. of coag. R. (6) R. with high V. gives a stronger vulcanizate. (8) Extraction of R. by acetone lowers V. by action of heat only. Returning the resin lowers the V. still further. Light lowers V.

Schidrowitz, P. (2) V. of R. and R. solutions. (3) Determination of V.

Schidrowitz, P. & Goldsbrough, H. A. (1) (3) V. tests on R. solutions.

Spence, D. & Kratz, G. D. (1) Trichloroacetic acid reduces the V. of a solution of R. in benzene.

Stevens, H. P. (1) Fractional separation of R. by solution and V. of the fractional solutions. (35) Viscous latex frequently yields a rapidly vulc. R. (58) V. of raw R. is an indication of the plasticity but high V. is not always accompanied by low plasticity.

Ultee, A. J. (4) HCHO added to latex gives R. of lowest V. and Na bisulfite gives highest V.  $\text{Na}_2\text{S}_2\text{O}_3$  decreases the V. of R. (7) V. determinations. (9) Fermented cocoanut water and coffee acid reduce the V. of R. Sugar as a coagulant reduces V. Papain gives slow drying R. of high V. Of the anti-coagulants bisulfite has the most favorable effect on V. (12) V. of crepe R. is dependent on the dilution of the latex at the time of coag.

deVries, O. (5) V. of R. decreases with increase of acid in coag. (16) No relation between V. and tensile, rate of vulc. or resistance to stretching.

Whitby, G. S. (8) p. 402. The value of V. determinations.

Woudstra, H. W. (1) V. of R. solutions decreases on standing.

#### “Vulcanisateur.”

Hutin, A. (2) See Dimethylamine-dimethylthiocarbamate.

#### Vulcanization.

Anon. (77) Effect of temp. on vulc. (78) Equivalent cures at various temperatures.

Bobet, R. (1) Vulc. is influenced by the nature of the crude R., amount of S., time, temp., etc. Vulc. R. contains only 1.5% Sc.

Bourne, A. O. (1) An increase of 11° F. doubles the velocity of vulc.

Kindscher, E. (2) Status of hot vulc. in 1922.

Ostromuiskii, I. (11) & (19) See Ageing-Oxidation.

Stevens, H. P. (22) R. containing 3-4% combined S is almost insol. in benzene.

Weber, C. O. (1) Vulc. takes place best at 258° F. or higher. (2) Concerning vulc. (1894). (23) Rate of vulc. dependent on heat conductivity and not on mechanical pressure.

#### Vulcanizing Agents.

See Antimony Sulfide, Sulfur Chloride, Chlorine, Disulfides, Nitrobenzene, etc.

Anon. (160) Vulc. in a hot solution of  $\text{K}_2\text{S}_2$ . (318) Vulc. with  $\text{S}_2\text{Cl}_2$ , bleaching powder and S., and  $\text{CaS}_2$  at 165° C.

Burke, W. H. (1) See Antimony Sulfide.

Gottlob, K. (10) p. 97. Vulc. properties of halogens, hypochlorites, selenium and tellurium.

Heinzerling, C. (1) p. 49. Vulc. by metallic sulfides.

Heyl, G. E. (1) Vulc. of R. with ground oil shale which contains S.

Ostromuiskii, I. (11) & (19) Attempts to vulc. R. by  $\text{As}_2\text{O}_3$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{CaCl}_2$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{KClO}_4$ ,  $\text{KAuO}_2$ ,  $\text{MnO}_2$  and  $\text{K}_3\text{Fe}(\text{CN})_6$ . (32) Vulc. of R. by an oxygen derivative of R.

Rodier, P. (1) Vulc. by chlorinated sulfuric acid chlorhydrin. See Chlorine.

Seeligmann, Torrilhon & Falconnet. (1) p. 163. In addition to S., the alkaline sulfides, several metallic sulfides and  $\text{S}_2\text{Cl}_2$  produce modifications in R. The halogens are more energetic in reacting with R. than S.

Sollier, F. (1) Vulc. with S bath,  $\text{K}_2\text{S}_2$  or  $\text{S}_2\text{Cl}_2$ .

Stevens, H. P. (73) Alternative methods of vulc.

#### Vulcanization-Coefficient.

See Sulfur-Coefficient.

#### Vulcanization-Discovery and History.

See Historical.

Geer, W. C. (5) Goodyear discovered vulc. of R. by S and white lead in Jan. 1839. Brookedon, an assistant of Hancock, first termed the process “vulcanization.”

Goodyear, Chas. (4) Vulc. of R. by heating with S and a carbonate or oxide of lead.

Hancock, T. (1) Early patent (1843) on vulc. by S. See Editorial (6) and Meyer, L. O. P. (12) for copy of pat. Meyer, L. O. P. (12) Description of Hancock's first work on vulc. and of his 14 patents.

Moulton, J. C. (1) Polemical with Nunn.

Nunn, J. H. (1) Polemical with J. C. Moulton.

Perkin, F. M. (1) History and theory of vulc.

Pickles, S. S. (5) Reply to J. H. Nunn.  
Schidrowitz, P. (46) History of vulc. and vulc. methods.

#### **Vulcanization-Methods.**

Anon. (79) Contrary to C. O. Weber, pressure exerts an accelerating action on vulc. (240) Reasons for longer time of vulc. necessary in hot air vs. steam. PbO prevents tackiness in dry heat.

Bernstein, G. (3) Vulc. by aid of ultra-violet light. See Light.

Bourn, A. O. (2) R. compounds vulc. in a heater with  $\text{NH}_4\text{Br}$ ,  $\text{NH}_4\text{I}$ , or  $(\text{NH}_4)_2\text{CO}_3$  which vaporize on heating. These compounds have an affinity for S. (4) Effect of time and temp. on the vulc. of R. by PbO and S.

Breuil, P. (16) Effect of time, temp., nature of the R. and temp. during testing on the physical properties of vulc. R.

Johnson, J. H. (1) Vulc. of R. by dipping in molten S.

Keene, C. (1) Vulc. of R. boots by exposure to fumes of S or dipped in molten S.

Kratz, G. D. (1) Effect of temp. on vulc.

Levy, A. (1) Vulc. with molten S or S in steam, air or press.

Spence, D. & Young, J. (3) Apparatus for experimental vulc. in a glycerine bath. Accurate control of time and temp.

Tagliabue, C. J. (1) Defects and remedies in vulc. methods.

Weber, C. O. (12) The longer time required in hot air vs. hot water cures is due to the coefficients of heat of the two media. (20) Circulation of air in hot air cures increases rate of vulc. (23) Pressure in dry heat cures does not increase rate of vulc.

#### **Vulcanization in Solution.** See Latex-Vulcanization.

Barus, C. (1) Solutions of vulc. R. by heating R. and S in  $\text{CS}_2$  to 200° C. under pressure.

Bedford, C. W. & Sebrell, L. B. (1) & (2) Vulc. of R. cements by S. and accels.

Blanc, M. le & Kröger, M. (1) Vulc. of R. in solution, with and without accels., by S,  $\text{S}_2\text{Cl}_2$ , SO, with  $\text{H}_2\text{S}$ , and nitro compounds.

Bloch, I. (1) Vulc. with  $\text{H}_2\text{S}$  in solution.

Boiry, F. (1) Vulc. of R. solutions at 120° C. Viscosity first diminishes then rapidly increases forming a gel followed by syneresis.

Heilbronner, A. & Bernstein, G. (3) See Light.

Hübener, G. (2) See Sulfur.

Peachey, S. J. (16) Vulc. of R. cements by S. and nitroso benzene.

leRoy, G. A. (1) See Phosphorous Thiobromide.

Stevens, H. P. (45) & (73) Vulc. of R. in sol and gel forms. The higher the amount of solvent the slower the vulc. Accels. may be used. See Sulfur Chloride and Trinitrobenzene.

Twiss, D. F. (11) Vulc. in solution by  $\text{S}_2\text{Cl}_2$  (Bernstein) and S. (Stern).

#### **Vulcanization at Low Temperatures.**

Bedford, C. W. & Scott, W. (1) Vulc. of R. cements.

Bedford, C. W. & Sebrell, L. B. (1) & (2) Vulc. of R. cements.

Bourn, A. O. (1) R.-100, PbO-50, S.-3 and chalk-50 was vulc. in 211 days at 40° C. and in 1 second at 333° C. (3) Para R. in S. at 110-115° F. contained 0.49% Sc. in 6 months.

Bruni, G. (3) Vulc. of R. at ordinary temp. by aniline,  $\text{CS}_2$ , ZnO and S. See Dithiocarbamates.

Bruni, G. & Romani, E. (1) & (3) Air curing of accels.

Hinrichsen, F. W. (3) Vulc. takes place slowly at 80° C. In presence of PbO appreciable amounts of combined S are formed in a few days. (4) Sc increases during storage of vulc. R.

Ostromuiskii, I. (14) & (31) Trinitrobenzene and PbO vulc. R. at ordinary temp. See Trinitrobenzene.

#### **Vulcanization-Theories.** See Colloid Chemistry of Rubber.

Alexander, P. (8) See Nitrosites.

Anon. (75) The nature of vulc. (79) Rate of vulc. is a function of temp.

- and accelerated by metallic oxides. (230) Vulc. begins below the m.p. of S.
- Arens, P. (1) Vulc. is dependent on the colloid structure of R.
- Axelrod, S. (1) Vulc. is accompanied first by depolymerization, later by polymerization.
- Bary, P. & Weydert, L. (1) The reversible nature of the vulc. process.
- Bedford, C. W. & Scott, W. (1) Reactions of accels. and polysulfide theory of vulc.
- Bedford, C. W. & Sebrell, L. E. (1) Carbosulphydryl accels. and the action of  $ZnO$ . (2) Mechanism of the action of zinc compounds.
- Bernstein, G. (2) Cold vulc. R. is a solid solution of the  $S_2Cl_2$  reaction product of R. in R. (5) S polymerizes R. Chemical reaction is a secondary process only. Sc is not a measure of vulc. Cold vulc. is a chemical reaction.
- Boggs, C. R. (3) The reaction products of accels. may constitute the actual vulc. agents (1914).  $PbO$  is an absorber for  $H_2S$ . Accels. affect combination of S as well as polymerization of R.
- Bruni, G. & Romani, E. (1) Mechanism of the action of certain accels.
- Budde, T. (4) Discussion of theories.
- Burghardt, C. A. (1) See Hydrogen Sulfide.
- Bysow, B. V. (3) Vulc. is not an exothermic process. A mix of R-100 and S-25 shows no elevation of temp. below  $150^\circ C$ . At  $180^\circ C$ . the temp. rises to  $225^\circ C$ . and  $H_2S$  is given off. Vulc. is wholly physical.
- Caspari, W. A. (1) Insoluble S is chemically combined with the R. (2) In favor of chemical reaction during vulc.
- Ditmar, R. (23) Theories of vulc. and the cyclo octadiene formula of Harries.
- Donath, E. (2) Vulc. R. is an alloy of R. and S or R. and metallic sulfides.
- Draper, W. F. (1) Comparison of the dyeing, tanning and vulc. processes. Adsorption theory.
- Dubosc, A. (1) (23) (30) (40) & (58) Metallic oxides and S form  $SO_2$  during vulc. Resins, proteins, org. accels., etc. with S form  $H_2S$ . The two gases interact to form active S which will vulc. R.  $SO_2 + 2H_2S = 2H_2O + S_2$ . Oxides, peroxides, carbonates, persulfates, plumbates and vanadium salts all shorten the time or lower the temp. of vulc. Higher alcohols, glycerine, terpeneol, phenols, etc. react with S during vulc. to give both  $H_2S$  and  $CS_2$  at high temp. It is preferable to use lanolin, etc., which generates  $H_2S$  at low temp. (7) Metallic sulfides do not dissociate at vulc. temp. to give S and do not vulc. R. (23) To bring about vulc. S must be colloidal. (28) Cold vulc. R. is  $(C_{10}H_{10})_2S_2Cl_2$  adsorbed in R. (29) Two stages of vulc. by S. Adsorption and chemical reaction. (39) Vulc. R. is a mixture of polyprene sulfide and unaltered metastable R. (62) Discussion of theories of Bary and Weydert, Erdmann, Potts, Stevens, Skellon, Loewen, L. E. Weber, van Rossem, van Iterson, etc.
- Editorial. (2) See Sulfur Chloride.
- Erdmann, H. (1) Thiozonide theory of vulc. See Sulfur.
- Esch, W. (2) Litharge and vulc. (6) History of vulc. and vulc. theories.
- Freundlich. (1) Adsorption equilibrium.
- Gaspari & Porritt. (1) Review of theories of vulc.
- Gibbons, W. A. (2) Review of literature on mechanism of vulc.
- Gottlob, K. (11) p. 71. part 2. Literature review.
- Harries, C. (31) p. 102.
- Henriques, R. (3) Vulc. R. contains an unvulc. portion of R.
- Hinrichsen, F. W. (2) Vulc. is a chemical process preceded by adsorption of S. The process is reversible. (5).
- Hinrichsen, F. W. & Kindscher, E. (4) Study of the end products of vulc. of R. by S. (6) Theories of vulc. by  $S_2Cl_2$ . (9) Vulc. is a chemical reaction.
- Hübener, G. (1) Chemical studies on ebonite.
- Hutin, A. (5) Accels. form unstable addition products with S which split off active S at vulc. temp.
- Iterson, G. van. (1) The nature of the vulc. process.
- Kimishima, T. (1) Vulc. of R. by disulfides and S due to liberation of

- active S from the reversible reaction  $R-S-S-R + H_2S = 2 R-S-H + S$ . See Thioaniline.
- Kirchhof, F. (2) Theory of vulc. and constitution of R.
- Loewen, H. (1) Discussion of theories of Ostwald and Spence. (2) See Sulfur. (3) Theories of vulc. Polemical with Stern (3).
- Minder, J. (4) Vulc. by S only takes place with S in the vapor state. S is slightly volatile at ordinary temp.
- Mueller, E. J. (1) Theory of vulc. by  $S_2Cl_2$ .
- Ostromuiskii, I. (12) Vulc. is a physical interaction of the colloid R. with a colloid vulc. agent. To be effective a vulc. agent must cause R. to swell in it. (15) Vulc. is a chemical reaction in which only a minute portion of the R. participates. Unchanged R. is adsorbed or swelled by the vulc. R. (17) Oxides cause S to react with amines forming trithiozonides which vulc. the R. and regenerate the amine. Amines and oxides lower the temp. of transformation of S to  $S_8$ .
- Ostwald, W. (1) & (2) Adsorption theory of vulc. (3) Vulc. is a physical process. Polemic with Spence & Young.
- Payen, M. (2) Vulc. is adsorption followed by chemical reaction.
- Potts, H. E. (1) Review of Ostwald, Stern, Hübener and Bysow on physical and chemical theories of vulc. (2) Adsorption theory of vulc. (3) Adsorption of S is followed by chemical reaction. (4) Review.
- Romani, E. (1) Thiuram disulfides as vulc. aids. (3) Action of dithioacids and nitrogen sulfide. (4) Aldehyde amines decompose during vulc. to the free aldehyde and amine.  $H_2S$  then forms polysulfides with the amines. The polysulfides change the aldehydes to dithioacids which in turn form zinc salts and then decompose into disulfides. The disulfides are the true vulc. agents.
- Rossem, A. van. (3) No relation between N content of R. and rate of vulc. (6) The vulc. process.
- Schidrowitz, P. (10) Vulc. is a progressive process which may be followed by stress-strain curves. (23) Vulc. R. is not a disulfide.
- Schidrowitz, P. & Goldsbrough, H. A. (9) Vulc. comprises two processes. A disintegration by heat and a "firming" by S.
- Seeligmann, Torrilhon & Falconnet. (1) p. 188. Review of theories of vulc.
- Seidl, E. (1) Action of  $PbO$  during hot vulc. Heat of reaction with S accelerates vulc.
- Skellon, H. (2) The rôle of polypropylene sulfide in vulc. (3) Migration of S and theory of vulc. See Sulfur.
- Spence, D. (19) Theory of vulc. (23) Polemical with Hinrichsen, Kindscher and Ostwald. (26) & (28) Vulc. accels.
- Spence, D. & Scott, J. H. (1) & (2) Theory of vulc. Chemical.
- Spence, D. & Ward, C. A. (1) Theory of vulc.
- Spence, D. & Young, J. (1) Vulc. is a chemical process. See Sulfur-Coefficient. (2) Vulc. of R., gutta percha and balata is a catalytic chemical reaction taking place at all temps. and proceeding to the same final product in the presence of excess of S.
- Stern, E. (2) Mechanism of the action of S. (3) Reversibility of vulc.
- Stevens, H. P. (22) Nature of vulc. (73) The typical properties of vulc. R. cannot be obtained without chemical combination.
- Tassilly, E. (1) p. 94 & 106. Vulc. by Se and halogens.
- Twiss, D. F. (4) The chemistry of vulc.
- Weber, C. O. (3) R. combines with S without evolution of  $H_2S$ . Vulc. is an addition process, forming a series of products from  $C_{100}H_{100}S$  to  $C_{100}H_{100}S_{20}$ . The physical constants of the R. colloid do not influence vulc. but affect the properties of the vulcanizate. (8) Absorption of S precedes vulc. Review of Höhn's work.
- Weber, L. E. (4) Vulc. is a chemical process which increases the degree of polymerization of the R.
- Zsigmondy, R. & Spear, E. B. (1) Theories of vulc.

"Vulcazol." See Furfuramide.

**"Vulcacite A."** See Aldehyde Ammonia.

Rossem, A. van. (6) Composition of.

**"Vulkacite P."** See Piperidine-pentamethylene-dithiocarbamate.

Anon. (307) Data on use in ebonite or soft R.

Dubosc, A. (40).

Gottlob, K. O. (7) Tabulations and graphs of vulc. tests.

Seidl, E. (4) Compounding data.

# **Water (Moisture).**

Anon. (161) Drying R. by evaporation of solvent from a gel.

Barclay, A. (1) Preservation of R. under water.

Bishop, R. O. (1) Variation in moisture content is without effect on the vulc. properties.

Brindejonc, G. (1) Action of sea water on Landolphia Hendelotii.

Dannerth, F. (6) Moisture produces blistering during vulc.

Eaton, B. J. (29) Wet R. does not deteriorate on storage.

Edwards, J. D. & Pickering, S. F. (1) Permeability of water thru R.

Hartjens, J. C. (3) Dilution of latex.

Miller, W. A. (1) Masticated R. absorbed 87% of its weight of water.

Payen, M. (1) Unvulc. R. absorbs 26% of its weight of water.

Rossem, A. van. (7) Water extract of Hevea R. 0.5 to 1.0%; of Para R. 0.4 to 0.5%. Evaporated latex gives higher extract.

le Roux. (1) R. swells slightly in water.

Schulze, E. (9) Vulc. R. takes up but little water. Unvulc. R. easily absorbs water. Effect on ageing.

Terry, H. L. (1) Adsorption of water by R. causes swelling and decreases adhesiveness. Pure R. standing in water undergoes slow decomposition.

deVries, O. (13) First latex crepe contains about 1% moisture. Smoked sheet 1.5%.

Whithy, G. S. (6) Moisture retaining capacity of raw rubber is closely related to the presence of serum solids which are hygroscopic.

**Waxes.** See Hydrogen Sulfide.

# **Whale Oil.**

Dubosc, A. (43) An accel. of vulc.

Murriel, P. I. (1).

# **White Lead.**

Geer, W. C. (5) p. 9 & 50. Historical.

Goodyear, Chas. (4) First use. See Tassilly (1) p. 214.

Grove, J. M. (1) Has same curing power, wt. for wt. as sublimed blue lead.

King, A. H. (1) Less toughening action than PbO.

Marzahn, R. (1) p. 467.

Pickles, S. S. (6).

# **Whiting.** See Calcium Carbonate.

Springer, G. (1) See Magnesium Carbonate.

# **"Xanthopone."** See Xanthates.

Anon. (100) A trade accelerator.

# **Xanthates.**

# **Xanthogenates.** See Cellulose Xanthate.

Bedford, C. W. & Sebrell, L. B. (1) Mentioned as accels. which are free from N.

Bruni, G. & Romani, E. (1) Mentions dixanthogens or oxidized xanthic acids. Zn ethylxanthate is a powerful accel.

Cadwell, S. M. (1) R.-100, ZnO-10, oxybutyl thiocarbonic acid disulfide-6, S-3, are mixed to form one stock. A second mix consists of R.-100, ZnO-10, S-3 and aniline-4. These stocks are blended, e.g., by passing through mixing rolls or by superposing thin sheets, and articles are made therefrom which are completely vulc. in a week at 70° F. Heat may be applied to shorten the vulc. time, but in this case the mixing should stand for a day to allow the vulc. ingredient to permeate the whole. The first stock may be merely exposed to aniline, or a stock containing aniline may be formed into articles which are then painted with butylthiocarbonic acid disulphide. For oxybutylthiocarbonic acid disulphide may be substituted oxyethyl, oxyamyl, oxy-methyl and like compounds, acetyl disulphide, benzoyl disulphide, and dithiobenzoyl disulphide, or the following xanthogenates, namely, mer-

curic ethyl, potassium amyl, zinc amyl, copper ethyl, zinc ethyl, barium ethyl, sodium methyl, lead methyl, zinc methyl, lithium ethyl, magnesium ethyl, calcium ethyl, potassium butyl, zinc butyl, potassium ethyl, sodium ethyl, lead ethyl. Aniline may be replaced by other amines such as ethylamine or paratoluidine. The whole of the ingredients in the example given are not essential for the carrying out of the process; when zinc butyl xanthogenate is employed, zinc oxide is not necessary, aniline and sulphur alone are necessary, or the aniline may be omitted and the vulc. carried out in the presence of zinc oxide and sulphur alone. Oxybutylthiocarbonic disulphide alone in sufficient quantity is a vulc. agent.

(2) Metallic xanthates, xanthic mono- and di-sulfides, dithiocarbamates, etc., as accels. Zn and Hg salts preferred for vulc. at low temps. For high temps. salts of the metals Zn, Hg, Pb, Cd, Cu, As and Mn are used. Bases and amines accel. the action of these substances. One-half mol of the amine should be used for each mol of  $CS_2$  in the thiol salt. Excess of aliphatic amine retards the vulc. The greater the amount of primary amine the greater the acceleration. R.-100, ZnO-10, Zn butyl-xanthate-4, S-1, toluidine-2. Vulc. takes place at ordinary temp. o-Normal-butylthiocarbonic acid disulfide and diphenyl-dimethyl-thiuramdisulfide also described as accels. (4) Na, Ba, Pb, Li, Mg, Ca,  $NH_4$ , K, ferric, mercuric and Zn salts of methyl or ethyl xanthates as accels. with or without the aid of amines. (5) & (6) As accels. of vulc. Metallic or amine salts of methyl, ethyl, amyl or other xanthates. Alkyl oxysters of thiol carbonates. Alkyl esters of thiocarbamic acids. Salts of mono- and dithio-acids. Thioamides. Salts and double ammonium salts of trithiocarbonic acids. Metallic salts of dithiocarbamic- and monothio-acids. Substituted thioureas. Esters of thiocarbonic acid disulfides and carbonyl disulfides. Thioacetyl sulfides and disulfides. Alkyl or aryl derivatives of thiuramdisulfides and mono

sulfides. Thio-acid-anhydrides. See Amines. (7) Benzoyl-butyl-(ethyl) xanthogenate, etc., as accels.

Geer, W. C. (3.)

Hoffman, H. A. (1) Zn amylxanthate in balata. Vulc. is started at  $215^\circ F$ . and completed at ordinary temp.

Ostromuiskii, I. (13) Zinc xanthates from glycerol, menthol, ethyl alcohol, isoamyl alcohol or terpineol as accels. (21) Mentioned. (22) Used in vulc. of synth. R.

Romani, E. (3) An atom of O substituted for S in the xanthates destroys their accel. power.

Twiss, D. F. (14) Zn xanthates are slow acting at  $148^\circ C$ . but very powerful at  $108^\circ C$ .

Twiss, D. F., Brazier, S. A. & Thomas, F. (1) Zn ethyl-xanthate is almost inactive in absence of ZnO. Does not vulc. R. in absence of S. Compounding data and graphs.

Winkelmann, H. A. & Gray, H. (1) The decomposition products of Zn ethyl-xanthate have no value as accels.

#### Xylidene.

Andrews, C. E. (1) An accel. of vulc. Bayer & Co. (24) 10% or more used as an elastifier for R. (32) Xylidene sulfate.

**Xylol Ether.** See Benzoyl Ether.

#### Zinc Borate.

Breuil, P. (6) Increases the hardness and elasticity of R.

#### Zinc Borocarbonate.

Lascelles-Scott, W. (29) Exerts a preservative influence on R.

#### Zinc Carbonate.

Breuil, P. (6) A R. pigment.

Meyer, L. O. P. (11).

Tyler, H. G. & Helm, J. G. (1) Used in R. in 1849.

#### Zinc Chloride.

Breuil, P. (6) Used by Brockedon for deodorizing R. C. Hancock treated raw gutta percha with  $NO_2$  and then plunged it in boiling  $ZnCl_2$  solution to improve its quality and lustre.

Weber, C. O. (6) Zn halides oxidize R. (38)  $ZnCl_2$  is deleterious to R.

**Zinc Dithiobenzoate.** See Dithioacids.

**Zinc Dithiopyromucate.** See Dithioacids.

**Zinc Hyposulfates.** See Hyposulfites.

Breuil, P. (6) R.-100, Zn hyposulfite-3. Vulc. for 5 hrs. at 125° C.

Marcy, E. E. (1) (2) (3) Vulc. with Zn hyposulfite without the use of S. aided by ZnS, PbS or PbCO<sub>2</sub>.

**Zinc Iodide (Bromide).** See Antimony Iodide.

Breuil, P. (6) Hancock used ZnI<sub>2</sub> as an accel. of vulc.

Fawsitt, C. A. (4) Vulc. of R. by S. with ZnI<sub>2</sub> and ZnBr<sub>2</sub>.

Marzahn, R. (1) p. 234. ZnI<sub>2</sub> used by Hancock.

**Zinc Mercaptides.** See Mercaptans.

Bedford, C. W. & Sebrell, L. B. (1) & (2) Zn salts of the mercapto form of thiocarbamilide are used to explain the curing power of this accel. Zinc thiophenol and other mercaptides mentioned.

**Zinc Mercapto-benzothiazole.** See Mercapto-benzothiazole.

**Zinc Oxide.**

Anon. (176). Use of ZnO and PbO in R.

Beadle, C. & Stevens, H. P. (4) ZnO changes to ZnS and ZnSO<sub>4</sub> during vulc.

Bedford, C. W. & Sebrell, L. B. (1) ZnO reacts during vulc. with mercaptans, dithiocarbamates or hydrogen sulfide to form accelerators which activate sulfur. (2) An aid to org. accels.

Breuil, P. (6) ZnO increases tensile of R. without decrease of extensibility.

Breyer, F. G. (1) A new ZnO of approximately the same size as gas black.

Brooks, B. T. (1) See p. 136. ZnO as an accel.

Bruni, G. (1) Zinc mercaptides and dithiocarbamates decompose during vulc. forming disulfides which vulc. R.

Cranor, D. F. (1) ZnO has a slight retarding action on the combination of S with R. See Sulfur-Coefficient.

Davies, E. L. (2) ZnO in R. compounds.

Ditmar, R. (20) See Ageing-Oxidation. (35) ZnO, PbO, MgO and BaSO<sub>4</sub> have no effect on the decomposition point of R.

Ditmar, R. & Thieben, R. (1) ZnO and S heated 45 min./4 atm. 72.6% of the ZnO changed to sulfides and sulfates. See Compounding Ingredients.

Dubosc, A. (6) ZnO does not increase tensile by its filling action but aids in the formation of colloidal S, thereby acting as an accel. (40) ZnO lacks curing power as its reaction with S is exothermic and no SO<sub>2</sub> is formed.

Gottlob, K. O. (6) p. 67. ZnO as an accel.

Heurn, F. C. van. (4) ZnO retards sulfuration of R.

Jones, F. (2) Mentions solution of ZnO in R. cements to a transparent gel.

Kratz, G. D. & Flower, A. H. (2) Large amounts of ZnO slightly increase the S. coefficient.

Kratz, G. D., Flower, A. H. & Coolidge, C. (1) Effect of ZnO on aniline and thiocarbamilide during vulc.

King, A. H. (1) ZnO has low accelerating power.

Luttringer, A. D. (2) See Magnesium oxide.

Marzahn, R. (1) See p. 487.

Maximoff, A. (1) ZnO is the most active oxide for use with thiuram mono- and di-sulfides.

Ostromuiskenskii, I. (21) & (25) ZnO accelerates the vulc. of R. by nitro compounds without S.

Pridham, J. (1) Use of ZnO in R. (1850).

Rosenbaum, J. L. (1) Effect of ZnO on org. accels.

Rossem, A. van. (6) Comparison of ZnO and other inorg. accels. by coefficient of vulc.

Scott, W. & Bedford, C. W. (1) ZnO reacts with thiocarbamilide to form the Zn salt of the mercapto form.

Tuttle, J. B. (1) ZnO should be used in all quality tests on crude R.

Twiss, D. F. (12) Effect of ZnO on org. accels. Discontinuity in elongation curves.



Twiss, D. F., Brazier, S. A. & Thomas, F. (1) ZnO enters into combination with org. accels. during vulc.

Twiss, D. F. & Howson, C. W. H. (17) Data and curves on effect of ZnO on org. accels.

Schidrowitz, P. (15) & (16) Modulus is affected by 0.5% ZnO without change in S. coefficient. (30) & (31) ZnO in crude R. tests.

Seidl, E. (1) Theory of heat of reaction of ZnO and S. to explain acceleration.

Stevens, H. P. (4) Estimation of ZnS and ZnSO<sub>4</sub> in vulc. R. (32) See Sulfur-Coefficient. (47) ZnO does not change the order of comparative value in crude R. tests. (51) Only a few "ultra accelerators" such as the dithiocarbamates are influenced by the presence of basic oxides. (70) Testing slab R. in ZnO and PbO mixings.

Weber, C. O. (45) Action of ZnO, PbO, etc. (1903).

Wilkens. (1) Absorption of ZnO from R. articles.

Williams, H. J. (1) Part II. ZnO changes to ZnS during vulc. (1892).

#### **Zinc Oxysulfate.**

Bolas, T. (3) Absorbs S and prevents bloom.

#### **Zinc Pentamethylene-dithiocarbamate.**

See Dithiocarbamates.

Bruni, G. (1) Causes vulc. with S. at temps. lower than 100° C.

Murrill, P. I. (5).

**Zinc Peroxide.** See Sulfur Dioxide.

#### **Zinc Phosphate.**

Breuil, P. (6) No value as a rubber pigment.

#### **Zinc Piperidyl-dithiocarbamate.**

See Zinc Pentamethylene-dithiocarbamate.

#### **Zinc Sulfide.**

##### **Zinc Polysulfide.**

Bedford, C. W. & Sebrell, L. B. (1) Mentions zinc polysulfide. (2) ZnS is an active accel. when properly prepared. ZNS<sub>x</sub> is an active curing agent.

Breuil, P. (6) Early use in R.

Ditmar, R. (47) p. 100. An accel. and an excellent pigment.

Esch, W. (7) ZnO does not form polysulfides during vulc. Gerard says ZnS acts as a S. carrier.

Gerner, H. (2) See Mercuric Sulfide.

Marcy, E. E. (2) See Zinc Hyposulfite.

Moulton, S. (1) & (2) See Hyposulfites.

Pearson, H. C. (1) p. 69. ZnS<sub>2</sub> loses its S. at too high a temp. to be used as a source of S for vulc.

Pickles, S. S. (6) An accel.

Tassilly, E. (1) p. 224. A white pigment that has some vulc. power.

Weber, C. O. (1) ZnS has some vulc. action.

#### **Zinc Bisulfite.**

##### **Zinc Sulfite.**

Heilbronner, A. (1) See Tannin.

Moulton, S. (2) A vulc. agent for R.

Rider, E. (1) See Hyposulfites.

**Zinc Sulfites.** See Hyposulfites.

**Zinc Thiocarbamilide.** See Mercaptans.

#### **Zinc Thiophenol.**

Bedford, C. W. & Sebrell, L. B. (1) An org. accel. free from N.

#### **Zirconium Oxide.**

Gardner, H. A. (1) A filler and an accel. for R.

# PATENT INDEX

## Australian Patents.

3,364 (1917)	Stowe, F. E.....	1
16,702 (1920)	Bedford, C. W. & Sibley, R. L.....	3
17,786 (1920)	Scott, W. ....	1

## Austrian Patents.

134 (1921)	Twiss, D. F. ....	2
1,429 ( )	Bayer & Co. ....	32
1,430 ( )	Bayer & Co. ....	34
2,464 (1905)	Morisse, L. P. T. ...	2
2,591 (1912)	Ostromuiskenskii, I. .	2
2,705 (1909)	Fisher, E. ....	1
3,830 (1905)	Frankel, M. & Runge	1
66,173 (1914)	Bayer & Co. ....	5
66,174 (1914)	Bayer & Co. ....	6
67,833 (1914)	Bayer & Co. ....	5
67,834 (1914)	Bayer & Co. ....	5
67,835 (1914)	Bayer & Co. ....	6
67,836 (1914)	Bayer & Co. ....	14
68,724 ( )	Bayer & Co. ....	14
69,974 (1915)	Bayer & Co. ....	19
76,012 ( )	Revere Rubber Co..	1
82,089 ( )	Bayer & Co. ....	33
82,803 (1921)	Collardon .....	1
82,807 (1915)	Peachey, S. J. ....	4
82,959 (1913)	Thomas, V. ....	1
83,052 (1921)	Heineman, A. ....	1
85,765 (1919)	Xylos Rubber Co. .	1
87,336 (1922)	Bayer & Co. ....	31
87,469 (1918)	Bayer & Co. ....	34
87,557 (1918)	Bayer & Co. ....	24
87,577 (1917)	Bayer & Co. ....	24
87,578 (1922)	Bayer & Co. ....	32
87,579 (1922)	Ungarische Gummi- warenfabriks .....	1
88,546 (1920)	Peachey, S. J. ....	14
88,547 (1921)	Peachey, S. J. ....	20
89,825 (1921)	Twiss, D. F. ....	2
90,775 (1922)	Kirchhof, F. ....	15

## Belgian Patents.

261,724 ( )	Bayer & Co. ....	6
261,870 ( )	Bayer & Co. ....	9
262,299 ( )	Bayer & Co. ....	14

## Canadian Patents.

167,204 (1916)	Murrill, P. I. ....	2
168,806 (1915)	Peachey, S. J. ....	4
168,807 (1915)	Peachey, S. J. ....	6
172,571 (1916)	Murdock, H. R. ....	1
179,352 (1917)	Ostromuiskenskii, I. .	25
179,353 (1917)	Ostromuiskenskii, I. .	28
179,354 (1917)	Ostromuiskenskii, I. .	31
179,355 (1917)	Ostromuiskenskii, I. .	30
179,356 (1917)	Ostromuiskenskii, I. .	26
179,379 (1917)	Ostromuiskenskii, I. .	21
180,003 ( )	Schidrowitz, P. & Goldsbrough, H. A. .	1
181,460 (1918)	Meyer, E. E. A. G...	1
181,461 (1918)	Whittelsey, T. T. ...	1
182,753 (1918)	Barton, L. E. & Gardner, H. A. ...	1
185,317 (1918)	Twiss, D. F. ....	2
188,135 (1918)	General Rubber Co..	5
188,136 (1918)	General Rubber Co..	1
188,137 (1918)	General Rubber Co..	2
190,042 (1919)	Twiss, D. F. ....	7
190,352 (1918)	Gibbons, W. A. ....	1
192,470 (1919)	Twiss, D. F. ....	6
193,394 (1919)	Thacker, S. P. ....	1
195,564 (1921)	Muntz, W. E. ....	3
196,143 (1920)	Sommerville, A. A. .	1
201,177 (1920)	Bedford, C. W. ....	1
204,387 (1920)	Porritt, B. D. ....	4
204,779 (1920)	Andrews, C. E. ....	1
205,728 (1920)	Ricard, E. ....	1
207,717 (1921)	Bedford, C. W. & Sibley, R. L. ....	2
207,718 (1921)	Scott, W. ....	1
207,719 (1921)	Bedford, C. W. ....	3
207,982 (1921)	Bedford, C. W. & Sibley, R. L. ....	2
207,983 (1921)	Bedford, C. W. & Sibley, R. L. ....	1
208,406 (1921)	O'Brien, W. J. ....	1
209,239 (1921)	Levinstein, E. ....	1
211,926 (1921)	Molony, S. B. ....	1
211,927 (1921)	Molony, S. B. & Ni- kaido, Y. ....	1
211,928 (1921)	Molony, S. B. & Ni- kaido, Y. ....	2
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219,474 (1922)	Lorentz, B. E. ....	1	2,188 (1797)	Johnson, H. ....	1
219,486 (1922)	Schidrowitz, P. ....	43	2,281 (1914)	Ripeau, E. ....	2
219,979 (1922)	Schidrowitz, Felden- heimer & Plow- mann .....	2	2,312 (1912)	Bayer & Co. ....	15
220,536 (1922)	Meyer, E. E. A. G. ....	2	2,313 (1912)	Bayer & Co. ....	15
223,831 (1922)	Cadwell, S. M. ....	3	2,541 (1866)	Forster, .....	1
223,992 (1922)	Hopkinson, E. ....	1	2,554 (1882)	Tour de Breuil ....	1
223,993 (1922)	Hopkinson, E. ....	2	2,706 (1879)	Spence, J. B. ....	1
224,110 (1922)	Bedford, C. W. & Sibley, R. L. ....	1	2,734 (1859)	Englehard, G. A. & Day, H. H. ....	1
227,316 (1923)	Weiss, M. L. ....	1	2,762 (1859)	Havemann, R. F. H.	1
228,725 (1923)	Weiss, M. L. ....	2	2,865 (1856)	Rider, E. ....	1
228,871 (1923)	Hartong, R. C. ....	1	2,982 (1904)	Leesman, L. & Wein- kopf, M. ....	1
228,873 (1923)	Bedford, C. W. ....	1	3,158 (1915)	Muntz, W. E. ....	1
			3,254 (1869)	Newbrough, J. B. & Fagan, E. ....	4
	<b>Ceylon Patents.</b>		3,940 (1909)	Immisch, O. C. ....	1
1,833 (1921)	Bamber, M. K. ....	6	4,263 (1914)	Peachey, S. J. ....	4
1,834 (1921)	Bamber, M. K. ....	6	4,451 (1820)	Hancock, Thos. ....	4
			4,692 (1906)	Schon & Son .....	1
	<b>English Patents.</b>		4,804 (1823)	Mackintosh, Chas. ..	1
20 (1911)	Clarkson, W. ....	1	4,910 (1913)	Muntz, W. E. ....	1
47 (1880)	Gerner, H. ....	1	4,955 (1914)	Muntz, W. E. ....	2
90 (1855)	Brooman, R. A. ....	1	5,018 (1824)	Weise, W. P. ....	1
166 (1878)	Abbott, W. ....	1	5,045 (1824)	Hancock, Thos. ....	8
178 (1856)	Johnson, W. ....	1	5,120 (1825)	Hancock, Thos. ....	5
190 (1881)	Mowbray .....	1	5,121 (1825)	Hancock, Thos. ....	9
305 (1866)	Turner, W. A. ....	2	5,430 (1912)	Badische Co. ....	4
394 (1888)	Wilhöf, F. ....	1	5,802 (1884)	White, N. S. ....	1
467 (1853)	Johnson, W. ....	1	5,846 (1829)	Harris, G. ....	1
477 (1853)	Symington, W. ....	1	5,970 (1830)	Hancock, Thos. ....	8
506 (1855)	Johnson, J. H. ....	1	6,046 (1835)	Sevier, R. W. ....	2
524 (1856)	Turner, W. A. ....	1	6,183 (1906)	Granier, E. & Froger- Delapierre, E. L. ...	1
537 (1871)	Warren, T. T. P. B.	1	6,232 (1882)	Gerner, H. ....	1
764 (1914)	Davidson, S. C. ....	4	6,344 (1898)	Ramsay, W. ....	1
787 (1881)	Rowley, T. ....	1	7,015 (1836)	Sievier, R. W. ....	1
931 (1922)	Naugatuck, Chem. Co. ....	1	7,159 (1901)	Bourn, A. O. ....	2
975 (1913)	Badische Co. ....	8	7,302 (1909)	Société Française de la Viscose .....	1
1,007 (1864)	Jennings, J. G. & Lavatier, M. L. J. ...	1	7,370 (1914)	Peachey, S. J. ....	2
1,111 (1914)	Schidrowitz, P. & Goldsbrough, H. A. ...	1	7,344 (1837)	Hancock, Thos. ....	6
1,124 (1911)	Bayer & Co. ....	3	7,694 (1905)	Morrisse, L. P. T. ...	1
1,207 (1910)	Smith, J. ....	1	7,823 (1915)	Oliver, H. P. M. A. ...	1
1,226 (1871)	Mackintosh, J. G. & Boggett, J. W. ....	1	8,487 (1915)	Ilcken, C. A. & Down, St. V. B. ...	2
1,254 (1908)	Fisher, E. ....	1	8,757 (1913)	Aylsworth, J. W. ...	1
1,445 (1911)	Heineman, A. ....	1	8,876 (1912)	Beyer, C. ....	1
1,499 (1859)	Barclay, A. ....	1	9,066 (1914)	Fulton, R. C. & MacCallum, D. A. ...	1
1,599 (1912)	Collardon, L. ....	1	9,189 (1841)	Fanshawe, J. A. ....	1
1,801 (1791)	Peal, S. ....	1	9,464 (1897)	Hornung, E. & Han- sel, S. ....	1
1,820 (1854)	Johnson, J. H. ....	2	9,665 (1922)	Edwardes, J. ....	1
1,894 (1915)	Peachey, S. J. ....	6	9,952 (1843)	Hancock, Thos. ....	1
2,070 (1914)	Matthews, F. E. & Strange, E. H. ....	1	9,956 (1908)	Degen & Kuth. ....	1
			10,027 (1844)	Goodyear, Chas. ....	1

10,056 (1911)	Rankin, R. ....	1	18,060 (1912)	Byrne, F. A. ....	1
10,361 (1910)	Ostwald, Wo. & Ostwald, Wa. ....	1	18,061 (1912)	Byrne, F. A. ....	1
10,458 (1887)	Griffin, J. T. ....	1	18,062 (1912)	Byrne, F. A. ....	3
10,692 (1845)	Keene, C. ....	1	18,269 (1908)	Wilderman, M. ....	1
10,883 (1914)	Peachey, S. J. ....	3	19,816 (1891)	Elworthy, H. S. ....	1
10,848 (1907)	Sandmann, D. ....	1	20,183 (1913)	Davidson, S. C. ....	4
10,990 (1845)	Thomson, R. W. ....	1	21,407 (1849)	Nickels ....	1
11,032 (1846)	Hancock, Chas. ....	2	22,138 (1914)	Davidson, S. C. ....	2
11,135 (1846)	Hancock, Thos. ....	7	22,607 (1909)	Scholz, V. ....	1
11,147 (1846)	Parkes, A. ....	1	23,723 (1911)	Badische Co. ....	1
11,159 (1899)	Marks, A. H. ....	1	23,727 (1910)	Beaver, C. J. & Clermont, E. A. ....	1
11,209 (1913)	Bayer & Co. ....	6	24,156 (1912)	Pahl, W. ....	2
11,273 (1912)	Davidson, S. C. ....	7	24,637 (1912)	Bayer & Co. ....	15
11,274 (1912)	Davidson, S. C. ....	8	24,795 (1912)	Pahl, W. ....	2
11,470 (1913)	Davidson, S. C. ....	5	24,848 (1898)	Zingler, M. ....	1
11,530 (1913)	Bayer & Co. ....	5 & 13	24,854 (1912)	Byrne, F. A. ....	2
11,567 (1847)	Moulton, S. ....	1	25,256 (1911)	Davidson, S. C. ....	7
11,575 (1847)	Hancock, Chas. ....	3	25,291 (1905)	Bamber, M. K. ....	2
11,576 (1910)	Thame, J. ....	1	25,573 (1910)	Livingston, G. B. & Cairney, W. D. ....	1
11,615 (1913)	Bayer & Co. ....	6	25,735 (1906)	Alexander, P. ....	6
11,615 (1915)	Baerveldt, J. F. ....	1	26,173 (1910)	Pahl, W. ....	2
11,874 (1847)	Hancock, Chas. ....	4	26,199 (1913)	Byrne, F. A. ....	4
12,077 (1847)	Hancock, Thos. ....	2	28,821 (1912)	Bayer & Co. ....	11
12,136 (1848)	Barlow, W. H. & Forster, T. ....	1	29,213 (1911)	Bayer & Co. ....	1
12,266 (1892)	Hutchinson, R. ....	2	34,613 (1922)	Pratt, W. B. ....	2
12,424 (1910)	Wilderman, M. ....	1	34,614 (1922)	Pratt, W. B. ....	2
12,591 (1849)	Burke, W. H. ....	1	101,819 (1916)	Peachey, S. J. ....	5
12,661 (1914)	Bayer & Co. ....	19	105,831 (1917)	Heyl, G. E. ....	1
12,777 (1913)	Bayer & Co. ....	14	108,298 (1911)	Lintner & Co. ....	1
12,815 (1913)	Badische Co. ....	6	108,300 (1916)	Ostromuiskenskii, I. ....	21
12,986 (1850)	Richards, Taylor & Wylde ....	1	108,453 (1916)	Ostromuiskenskii, I. ....	26
13,062 (1850)	Siemens, E. W. ....	1	110,059 (1917)	Twiss, D. F. ....	2
13,170 (1850)	Goodyear, Chas. ....	1	111,257 (1917)	Barton, L. E. & Gardner, H. A. ....	1
13,226 (1893)	Hutchinson, R. ....	2	111,907 (1916)	Ilcken, C. A. & Down, St. V. B. ....	1
13,438 (1913)	Davidson, S. C. ....	4	113,570 (1917)	Peachey, S. J. ....	9
13,542 (1851)	Goodyear, Chas. ....	1	114,373 (1918)	Bayles, E. A. ....	1
13,570 (1909)	Schon & Son ....	1	116,322 (1917)	General Rubber Co. ....	7
13,721 (1851)	Moulton, S. ....	2	116,323 (1917)	General Rubber Co. ....	1
14,355 (1914)	Bradley, W. P. ....	1	116,324 (1917)	General Rubber Co. ....	2
14,681 (1905)	Alexander, P. ....	6	116,326 (1917)	General Rubber Co. ....	5
16,096 (1914)	Mosinger, E. ....	2	121,091 (1917)	Peachey, S. J. ....	6
16,352 (1912)	Davidson, S. C. ....	6	121,194 (1918)	Peachey, S. J. ....	14
16,663 (1909)	Poizot, E. ....	1	124,276 (1918)	Twiss, D. F. ....	7
16,728 (1913)	Berry, A. E. & Boake, A. ....	1	124,887 (1919)	Porzel, J. ....	1
16,971 (1908)	Rutgers Werke ....	1	125,695 (1919)	Twiss, D. F. ....	6
17,195 (1913)	Bernstein, G. ....	1	125,696 (1919)	Twiss, D. F. ....	6
17,197 (1890)	Fawsitt, C. A. ....	4	126,236 (1918)	Leheup, C. E. ....	1
17,367 (1920)	Pratt, W. B. ....	1	126,397 (1917)	Spence, D. ....	27
17,677 (1912)	Spence, D. & Russell, W. F. ....	1	126,606 (1919)	Hasselt, J. F. B. Van	1
17,739 (1893)	Hutchinson, R. ....	1	127,481 (1918)	Broadhurst, Lamble & Peachey ....	1
17,760 (1915)	Twiss, D. F. ....	2	129,429 (1921)	Peachey, S. J. ....	20
17,830 (1912)	Bayer & Co. ....	10	129,798 (1919)	Porritt, B. D. ....	4

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129,826 (1919)	Peachey, S. J. ....	14	177,787 (1922)	Gibbons, W. A. & Ritter, H. W. ....	1
130,857 (1919)	Bedford, C. W. ....	1	178,337 (1922)	McGuire, A. G. & Coulter & Davidson	1
136,716 (1919)	Peachey, S. J. ....	15	178,796 (1922)	Geer, W. C. ....	3
140,387 (1920)	Bruni, G. ....	1	180,978 (1922)	Cadwell, S. M. ....	3
140,388 (1920)	Bruni, G. ....	1	181,365 (1922)	Moureaux, C. & Dufrasse, C. ....	1
141,412 (1919)	Gaismann, L. & Rosenbaum, J. L. .	1	183,922 (1921)	Frood, F. & Alger, H. P. ....	1
142,083 (1920)	Heilbronner, A. ...	1	184,578 (1921)	Brittain, P. ....	1
142,801 (1920)	Ose, Y. ....	1	186,671 (1922)	Jones, F. C. ....	4
143,610 (1919)	Hartong, R. C. ....	1	188,008 (1921)	Lebeuvre, C. ....	1
146,734 (1919)	Peachey, S. J. ....	16	190,051 (1922)	Peachey, S. J. ....	26
146,992 (1920)	Bedford, C. W. ....	3	190,099 (1922)	General Rubber Co.	12
148,349 (1920)	Tilche, E. ....	1	190,510 (1922)	Reid, Chas. ....	1
148,350 (1920)	Tilche, E. ....	1	191,085 (1922)	Cadwell, S. M. ....	8
153,343 (1919)	Schidrowitz, Feldenheimer & Plowmann	1	193,451 (1923)	Schidrowitz, ....	52
153,890 (1921)	Scott, W. ....	1	<b>Federated Malay States Patents.</b>		
156,118 (1920)	Plauson, H. & Vielle, J. A. ....	1	2 (1916)	Ilcken, C. A. & Down, St. V. B. ...	1
157,050 (1920)	Ricard, E. ....	1	8 (1922)	Schidrowitz, P. ....	52
157,821 (1921)	India Rubber, Gutta Percha & Telegraph Works	1	12 (1915)	Davidson, S. C. ...	3
157,975 (1921)	Hopkinson, E. ....	1	13 (1915)	Davidson, S. C. ...	4
157,978 (1921)	Hopkinson, E. ....	2	16 (1915)	Ilcken, C. A. & Down, St. V. B. ...	2
159,014 (1919)	Perkin, W. H. & Mandelberg, J. H. .	1	17 (1915)	Davidson, S. C. ...	4
159,602 (1919)	Davidson, S. C. ...	1	17 (1917)	Ilcken, C. A. & Down, St. V. B. ...	3
160,499 (1921)	Peachey, S. J. & Skipsey, A. ....	1	18 (1916)	Ilcken, C. A. & Down, St. V. B. ...	4
161,482 (1920)	O'Brien, W. J. ....	1	18 (1921)	Laub, G. C. H. ....	1
161,483 (1920)	North, C. O. ....	1	19 (1921)	Laub, G. C. H. ....	2
162,429 (1921)	Peachey, S. J. ....	20	25 (1917)	General Rubber Co.	1
162,528 (1920)	Stevens, H. P. ....	43	26 (1917)	General Rubber Co.	2
164,326 (1921)	Kelly, W. J. & Smith, C. H. ....	1	27 (1917)	General Rubber Co.	3
164,770 (1920)	Stevens, H. P. ....	45	28 (1917)	General Rubber Co.	4
166,731 (1920)	Schidrowitz, P. ....	51	29 (1917)	General Rubber Co.	5
170,682 (1921)	Schidrowitz, P. ....	43	30 (1917)	General Rubber Co.	6
171,046 (1920)	Bilbrough, C. F. S. .	1	34 (1917)	General Rubber Co.	8
171,803 (1922)	Speedy, A. & Crouch, A. P. ....	1	35 (1917)	General Rubber Co.	9
172,711 (1921)	Schidrowitz, Feldenheimer & Plowmann	2	109 (1912)	Byrne, F. A. ....	1
172,754 (1921)	Peachey, S. J. & Skipsey, A. ....	3	<b>French Patents.</b>		
173,545 (1922)	Bedford, C. W. & Sibley, R. L. ....	2	16,938 (1912)	Bayer & Co. ....	11
173,546 (1922)	Bedford, C. W. & Sibley, R. L. ....	3	18,428 (1913)	Bayer & Co. ....	7
174,915 (1922)	Cadwell, S. M. ....	1	18,705 (1913)	Bayer & Co. ....	14
177,493 (1922)	Cadwell, S. M. ....	2	19,455 (1915)	Bayer & Co. ....	19
177,495 (1922)	Hug, E. ....	1	22,779 (1921)	Bruni, G. ....	1
177,566 (1922)	Peachey, S. J. ....	23	215,549 (1891)	Fawsitt, C. A. ....	5
			220,520 (1892)	Raymond, J. M. ...	1
			329,519 (1903)	Geoffroy & Delore, G. ....	1
			355,017 ( )	Germain, P. ....	1
			358,018 (1905)	Alexander, P. ....	6

360,324 (1905)	Morisse, L. P. T. . .	1	485,975 (1918)	Barton, L. E. & Gardner, H. A. . .	1
360,325 (1906)	Morisse, L. P. T. . .	2	488,036 (1917)	Twiss, D. F. . . . .	6
372,771 (1907)	Granier, L. & Froger-Delapierre, E. L. .	1	490,897 (1914)	Peachey, S. J. . . . .	5
377,526 (1907)	Sandmann, D. . . . .	1	490,965 (1918)	Peachey, S. J. . . . .	9
380,998 (1906)	Guerry, L. . . . .	1	492,140 (1922)	Bedford, C. W. . . . .	1
386,017 (1908)	Fisher, E. . . . .	1	493,634 (1919)	Twiss, D. F. . . . .	7
390,637 (1907)	Basler, J. . . . .	1	494,757 (1917)	Spence, D. . . . .	27
393,186 (1908)	Rutgers Werke . . . .	1	495,284 (1919)	Hasselt, J. F. B. van	1
395,101 (1908)	Wildermann, M. . . .	1	496,220 (1918)	Porritt, B. D. . . . .	4
401,303 (1908)	Poizot, E. . . . .	1	497,327 (1920)	Twiss, D. F. . . . .	2
404,307 (1909)	General Caoutchouc Co., Ltd. . . . .	1	505,701 (1921)	Compagnie Parisienne des Tissus Caoutchouc. . . . .	1
410,332 (1910)	Anon. . . . .	34	510,197 (1919)	Tilche, E. . . . .	1
411,993 (1910)	Smith, J. . . . .	1	516,304 (1920)	Peachey, S. J. . . . .	19
415,177 (1910)	Benjamin, E. . . . .	1	520,329 (1920)	Bedford, C. W. . . . .	5
419,281 (1910)	Paulet, F. . . . .	1	520,330 (1920)	Bedford, C. W. . . . .	3
435,076 (1911)	Bayer & Co. . . . .	4	520,331 (1920)	Hartong, R. C. . . . .	1
438,778 (1912)	Eichelbaum, G. . . . .	1	520,332 (1920)	Bedford, C. W. & Sibley, R. L. . . . .	2
439,101 (1912)	Heineman, A. . . . .	1	520,477 (1920)	Bruni, G. . . . .	1
441,204 (1912)	Badische Co. . . . .	5	521,884 (1920)	North, C. O. . . . .	1
441,477 (1912)	Bayer & Co. . . . .	3	523,417 (1920)	Ricard, E. . . . .	1
441,568 (1912)	Beyer, C. . . . .	1	525,268 (1920)	Scott, W. . . . .	1
442,331 (1912)	Beyer, C. . . . .	1	525,580 (1920)	Stevens, H. P. . . . .	45
443,018 (1912)	Bouffort, M. M. J. . .	1	526,533 (1920)	Schidrowitz, Feldenheimer & Plowmann . . . . .	1
446,224 (1911)	Reynaud, G. . . . .	2	526,882 (1920)	Sistron, X. F. . . . .	1
446,598 (1912)	Bayer & Co. . . . .	15	529,327 (1921)	Hopkinson, E. . . . .	2
446,692 (1915)	Lumiere . . . . .	1	532,450 (1922)	Dunlop Rubber Co. .	1
448,974 (1912)	Spence, D. & Russell, W. F. . . . .	1	533,198 (1921)	Bedford, C. W. & Sibley, R. L. . . . .	3
450,567 (1912)	Bayer & Co. . . . .	12	536,733 (1921)	Bernstein, G. . . . .	9
452,688 (1912)	Reynaud, G. . . . .	3	541,146 (1921)	Peachey, S. J. & Skipsey, A. . . . .	3
453,394 (1913)	Collardon, L. . . . .	1	543,217 (1921)	Fleury, R. de . . . . .	2
459,134 (1913)	Matthews, F. E. . . . .	1	543,503 (1922)	Hug, E. . . . .	1
460,780 (1913)	Thomas, V. . . . .	1	<b>German Patents.</b>		
462,156 (1912)	Anquetil, C. E. . . . .	1	2,265 (1878)	Abbott, W. . . . .	1
463,437 (1913)	Badische Co. . . . .	6	10,450 ( )	Gerner, H. . . . .	1
464,192 (1913)	Boehringer, C. H. & Sohn . . . . .	1	14,588 (1894)	Hutchinson, R. . . .	1
464,533 (1913)	Bayer & Co. . . . .	5 & 6	18,740 (1881)	Kreussler, U. & Budde, E. . . . .	1
466,243 (1913)	Xylos Rubber Co. . . .	1	22,359 ( )	Tour de Breuil . . .	1
468,493 (1914)	Muntz, W. E. . . . .	1	24,870 (1883)	Gerner, H. . . . .	1
470,833 (1913)	Bastide . . . . .	1	25,292 (1907)	Rutgers Werke . . .	1
473,110 (1914)	Grieschein-Elektron Chem. Fabr. . . . .	1	28,467 (1922)	Esch, W. . . . .	16
474,078 (1914)	Revere R. Co. . . . .	1	33,496 ( )	Bayer & Co. . . . .	39
475,601 (1914)	Ostromuiskenskii, I. .	22	34,143 ( )	Bayer & Co. . . . .	28
476,059 (1914)	Rodier, P. . . . .	1	43,563 (1922)	Bayer & Co. . . . .	40
477,204 (1914)	Oliver, H. P. M. A. . .	1	67,255 ( )	Bouchardat, M. G. & Lafont, J. . . . .	2
477,586 (1915)	Peachey, S. J. . . . .	4	74,928 (1893)	Hutchinson, R. . . .	1
480,904 (1916)	Peachey, S. J. . . . .	6	77,856 (1894)	Hutchinson, R. . . .	2
483,207 (1917)	Estruch, E. de L. . . .	1			
484,536 (1918)	Magen, A. A. . . . .	1			
485,778 (1919)	General Rubber Co. . .	10			
485,791 (1918)	General Rubber Co. . .	2			
485,797 (1918)	General Rubber Co. . .	6			
485,827 (1918)	General Rubber Co. . .	1			

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85,671 (1918)	Badische Co. ....	9	272,995 (1912)	Davidson, S. C. ....	7
97,113 (1897)	Hornung, E. & Hansel, S. ....	1	273,482 (1912)	Esch, W. ....	13
104,356 ( )	Zingler, M. ....	1	273,774 (1913)	Ephraim, J. ....	1
176,661 (1905)	Morisse, L. P. T. ..	1	275,716 (1912)	Boehringer, C. H. & Sohn ....	1
183,648 (1904)	LeRoy, G. A. ....	1	276,775 (1913)	Badische Co. ....	7
189,235 (1906)	Sandmann, D. ....	1	276,780 (1913)	Badische Co. ....	8
197,154 (1906)	Frankel, M. & Runge	1	276,960 (1913)	Badische Co. ....	6
200,667 (1906)	Frankel, M. & Runge	1	277,549 (1913)	Condensite Co. of America ....	1
201,121 (1907)	Fölsing ....	1	278,874 (1912)	Spence, D. & Russell, W. F. ....	1
205,886 (1909)	Degen & Kuth ....	1	279,271 (1911)	Lamberty, E. ....	1
210,116 (1907)	Ozenne, C. ....	1	279,780 (1914)	Badische Co. ....	8
211,186 (1907)	Fisher, E. ....	1	280,198 (1914)	Bayer & Co. ....	19
214,518 (1909)	Rutgers Werke ....	1	280,848 (1913)	Colloseus, H. ....	1
216,277 (1909)	Wilderman, M. ....	1	282,128 (1913)	Traun, H. ....	2
218,225 (1908)	Chercheffsky, N. ..	2	283,111 (1913)	Heuser, E. & Boedecker, G. ....	1
219,525 (1908)	Bloch, I. ....	1	290,808 (1914)	Bayer & Co. ....	20
221,310 (1908)	Ostwald, Wo. & Ostwald, Wa. ....	1	301,757 (1915)	Bayer & Co. ....	24
223,080 (1910)	Reithofer, J. N. ....	1	303,224 (1916)	Bayer & Co. ....	27
224,040 (1907)	Rutgers Werke ....	1	303,966 (1916)	Bayer & Co. ....	28
228,858 (1910)	Chercheffsky, N. ..	1	303,984 (1917)	Bayer & Co. ....	31
234,552 (1909)	Poizot, E. ....	2	305,667 (1917)	Bayer & Co. ....	32
237,789 (1910)	Pahl, W. ....	2	312,831 (1912)	Heinemann, A. ....	1
243,248 (1911)	Beyer, C. ....	1	315,321 (1918)	Peter, L. ....	1
243,346 (1909)	Ostwald, Wo. & Ostwald, Wa. ....	1	316,009 (1917)	Bayer & Co. ....	29
250,920 (1911)	Bayer & Co. ....	15	320,016 (1913)	Xylos Rubber Co. ..	1
254,196 (1911)	Eichelbaum, G. ...	1	320,170 ( )	Byrne, F. A. ....	1
254,548 (1910)	Bayer & Co. ....	4	321,092 (1914)	Schidrowitz, P. & Goldsbrough, H. A. ..	1
255,680 (1911)	Bayer & Co. ....	15	323,088 (1915)	Peachey, S. J. ....	4
256,216 (1912)	Pahl, W. ....	2	323,732 (1918)	Ungarische Gummiwaren-Fabriks ..	1
256,413 (1911)	Bayer & Co. ....	42	325,306 (1919)	Hasselt, J. F. B. van	1
256,904 (1911)	Eichelbaum, G. ...	1	326,819 (1917)	Bayer & Co. ....	33
257,813 (1911)	Bayer & Co. ....	1	328,610 (1917)	Bayer & Co. ....	34
259,253 (1912)	Colloseus, H. ....	2	328,611 (1920)	Peachey, S. J. ....	4 & 5
259,722 (1912)	Bayer & Co. ....	11	329,293 (1916)	Peachey, S. J. ....	6
260,916 (1912)	Klopstock, H. ....	1	330,741 (1918)	Badische Co. ....	9
262,093 (1911)	Reynaud, G. ....	1	331,031 (1917)	Accumulator Fabrik Akt. Ges. ....	1
262,563 (1912)	Boehringer, C. H. & Sohn ....	2	332,305 (1918)	Badische Co. ....	10
262,708 (1912)	Bernstein, G. ....	1	332,347 (1921)	Bayer & Co. ....	38
264,820 (1911)	Bayer & Co. ....	2	332,974 (1919)	Meßzeler & Co. ....	1
265,221 (1912)	Bayer & Co. ....	5	333,496 (1921)	Badische Co. ....	11
266,153 (1912)	Bayer & Co. ....	2	340,491 (1920)	Twiss, D. F. ....	2
266,618 (1912)	Bayer & Co. ....	7	343,181 (1920)	Peachey, S. J. ....	14
266,619 (1912)	Bayer & Co. ....	6	344,061 (1919)	Esch, W. ....	16
267,277 (1912)	Harries, I. C. ....	21	345,160 (1917)	Bayer & Co. ....	35
267,945 (1912)	Bayer & Co. ....	8	349,699 (1919)	Deutsche - Peerless Ges. ....	1
267,903 (1912)	Harries, I. C. ....	21	351,785 (1922)	Plauson, H. ....	1
267,994 (1912)	Harries, I. C. ....	21	351,974 (1922)	Peachey, S. J. ....	9
268,387 (1912)	Bayer & Co. ....	9	354,172 (1920)	Bayer & Co. ....	37
268,843 (1912)	Hutz, H. ....	1	354,344 (1920)	Siemens & Halske. ..	1
268,947 (1914)	Bayer & Co. ....	13			
269,512 (1913)	Bayer & Co. ....	14			
271,849 (1912)	Badische Co. ....	2			
272,399 (1912)	Badische Co. ....	3			

358,729 (1922)	Siemens & Halske.	2	9,891 (1853)	Norris, H. L. ....	1
362,667 (1922)	North British Rubber Co. ....	1	11,897 (1854)	Marcy, E. E. ....	4
366,114 (1922)	Bayer & Co. ....	41	18,479 (1910)	Clarkson, W. ....	1
369,592 (1920)	Schidrowitz, Feldenheimer & Plowmann ....	2	24,695 (1859)	Eaton, A. K. ....	1
375,776 (1922)	Esch, W. ....	18	25,271 (1859)	Marcy, E. E. ....	1
			25,272 (1859)	Marcy, E. E. ....	2
			25,273 (1859)	Marcy, E. E. ....	3
			25,957 (1859)	Dieffenbach, G. ...	1
			26,175 (1859)	Englehard, G. A. & Havemann, R. F. H. ....	1
	<b>Holland Patents.</b>		26,358 (1859)	Marcy, E. E. ....	3
1,204 (1912)	Eichelbaum, G. ....	2	26,359 (1859)	Marcy, F. E. ....	1
2,072 (1917)	Kerbosch, M. ....	6	26,360 (1859)	Marcy, E. E. ....	2
2,150 (1917)	Colloseus, H. ....	1	27,798 (1860)	Harris, C. T. ....	1
2,829 (1919)	Peachey, S. J. ....	4	28,744 (1860)	Eaton, A. K. ....	2
17,924 (1923)	Hopkinson, E. ....	2	30,807 (1860)	Falke, O. & Richards, A. C. ....	1
	<b>Italian Patents.</b>		31,240 (1861)	Havemann, R. F. H. ....	1
139,536 (1914)	Bayer & Co. ....	22	31,241 (1861)	Havemann, R. F. H. ....	1
173,322 (1918)	Bruni, G. ....	1	42,662 (1864)	Ayling, H. A. ....	1
173,364 (1919)	Bruni, G. ....	1	42,663 (1864)	Ayling, H. A. ....	1
449,101 (1915)	Oliver, H. P. M. A. ....	1	51,331 (1865)	Reissue (1866) Marquard, F. ....	1
	<b>Japanese Patents.</b>		51,332 (1865)	Reissue (1866) Marquard, F. ....	2
31,500 (1917)	Sumitomo, K. ....	1	70,250 (1867)	Newbrough, J. B. & Fagan, E. ....	4
34,944 (1919)	Twiss, D. F. ....	6	73,545 (1868)	Newbrough, J. B. & Fagan, E. ....	1
36,754 (1920)	Shirai, Tanaka & Yosikawa ....	1	73,916 (1868)	Newbrough, J. B. & Fagan, E. ....	2
	<b>New Zealand Patents.</b>		73,917 (1868)	Newbrough, J. B. & Fagan, E. ....	3
44,002	Peachey, S. J. ....	14	84,369 (1868)	Newbrough, J. B. ....	1
	<b>Norway Patents.</b>		100,435 (1870)	Newbrough, J. B. ....	2
31,969 (1921)	Peachey, S. J. ....	20	218,842 (1879)	Watles, J. W. ....	1
	<b>Russian Patents.</b>		236,240 (1881)	Mowbray, J. M. ....	1
70,011 (1916)	Maximoff, A. ....	2	247,834 (1881)	Mayall, T. J. ....	1
	<b>Straits Settlements Patents.</b>		255,139 (1882)	Burr, H. W. ....	1
1,033 (1922)	Brereton, C. A. ....	1	308,189 (1884)	Montgomery, J. J. ....	1
1,038 (1922)	Bunker, S. W. ....	1	321,410 ( )	Wilhöft, F. ....	2
	<b>Swiss Patents.</b>		375,405 (1887)	Wilhöft, F. ....	1
66,133 ( )	Thomas, V. ....	1	438,309 (1890)	Edison, T. A. ....	1
90,484 (1921)	Peachey, S. J. ....	14	490,500 (1893)	Raymond, J. M. ....	1
	<b>United States Patents.</b>		538,147 (1895)	Barus, C. ....	1
240 (1837)	Goodyear, Chas. ...	5	621,060 (1899)	Garnier, E. ....	1
1,090 (1839)	Hayward, N. ....	1	657,240 (1900)	Hornung, E. & Hansel, S. ....	1
3,633 (1844)	Reissue 156 (1849) Goodyear, Chas. .	1	680,387 (1901)	Moore, L. R. ....	1
8,075 (1851)	Goodyear, Nelson	1	697,792 (1902)	Bourn, A. O. ....	2
9,246 (1852)	Bronner, F. ....	1	837,865 (1906)	Morgan, H. W. ..	1
			841,394 (1906)	Alexander, P. ....	6



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844,077 (1907)	Alexander, P. ....	6	1,248,888 (1917)	Badische Co. ....	6
853,718 (1907)	Morisse, L. P. T. ...	1	1,249,180 (1917)	Ostromuiskenskii, I.	25
859,611 (1907)	Morisse, L. P. T. ...	2	1,249,181 (1917)	Ostromuiskenskii, I.	27
906,306 (1909)	Scherpe, H. ....	1	1,249,272 (1917)	Boggs, C. R. ....	1
910,520 (1908)	Fischer, E. ....	1	1,254,632 (1918)	Snyder, E. W. ....	1
935,414 (1909)	Sandmann, D. ....	1	1,256,496 (1918)	Oliver, H. P. M. A.	1
937,745 (1909)	Immisch, O. C. ....	1	1,259,793 (1918)	General Rubber	
963,806 (1910)	Poizot, E. ....	1		Co. ....	5
1,022,014 (1912)	Wilderman, M. ...	1	1,259,794 (1918)	General Rubber	
1,032,428 (1912)	Reynaud, G. ....	4		Co. ....	1
1,035,788 (1912)	Heinemann, A. ...	1	1,268,639 (1918)	General Rubber	
1,039,741 (1912)	Bayer & Co. ....	3		Co. ....	6
1,051,987 (1915)	Chute, H. O. ....	2	1,269,168 (1918)	Fahrenwald, F. A.	1
1,076,106 (1913)	Bayer & Co. ....	16	1,270,887 (1918)	General Rubber	
1,081,613 (1913)	Bayer & Co. ....	15		Co. ....	9
1,081,614 (1913)	Bayer & Co. ....	15	1,271,810 (1918)	Twiss, D. F. ....	2
1,084,335 (1913)	Bayer & Co. ....	17	1,280,940 (1918)	Andrews, C. E. ...	1
1,084,336 (1913)	Bayer & Co. ....	17	1,288,723 (1918)	Snelling, W. O. ...	1
1,084,337 (1913)	Bayer & Co. ....	18	1,289,566 (1918)	Somerville, A. A.	
1,084,338 (1913)	Bayer & Co. ....	17		& Rentschler, M.	
1,098,882 (1914)	Collardon, L. ....	1		J. ....	1
1,112,938 (1914)	Spence, D. & Rus-		1,291,828 (1919)	Gibbons, W. A. ...	1
	sell, W. F. ....	1	1,296,469 (1919)	Boggs, C. R. ....	3
1,113,614 (1914)	Bayer & Co. ....	10	1,301,693 (1919)	Hartong, R. C. ...	3
1,113,630 (1914)	Bayer & Co. ....	21	1,304,777 (1920)	Kryder, F. L. ....	1
1,113,759 (1914)	Ditmar, R. ....	58	1,306,838 (1919)	General Rubber	
1,122,653 (1914)	Spence, D. ....	24		Co. ....	2
1,126,469 (1915)	Bayer & Co. ....	6	1,309,703 (1919)	Somerville, A. A.	1
1,128,851 (1915)	Collardon, L. ....	1	1,312,007 (1919)	Thierfelder, R. E.	
1,130,736 (1915)	Jewett, I. D. ....	1		& Schmaelzle, R.	1
1,130,903 (1915)	Bayer & Co. ....	14	1,312,144 (1919)	Thacker, S. P. ....	1
1,136,462 (1915)	Bary, P. ....	5	1,320,166 (1919)	Ostromuiskenskii, I.	21
1,145,351 (1915)	Davidson, S. C. ...	7	1,321,501 (1919)	Bedford, C. W. ...	5
1,145,352 (1915)	Davidson, S. C. ...	5	1,322,518 (1919)	Barton, L. E. ....	1
1,146,851 (1915)	Davidson, S. C. ...	3	1,322,734 (1919)	Smith, H. E. ....	1
1,149,580 (1915)	Bayer & Co. ....	19	1,323,951 (1919)	Bedford, C. W. ...	3
1,156,184 (1915)	Schidrowitz, P. &		1,326,319 (1919)	Barton, L. E. &	
	Goldsbrough, H.			Gardner, H. A. ...	1
	A. ....	1	1,332,925 (1920)	General Rubber	
1,157,177 (1915)	Peachey, S. J. ....	4		Co. ....	3
1,159,327 (1915)	Murrill, P. I. ....	1	1,332,926 (1920)	General Rubber	
1,166,777 (1916)	Murrill, P. I. ....	3		Co. ....	8
1,182,501 (1916)	Murrill, P. I. ....	2	1,340,777 (1920)	Kryder, F. L. ....	1
1,184,015 (1916)	Price, R. B. ....	1	1,341,423 (1920)	Gegenheimer, R.	
1,203,241 (1916)	Muntz, W. E. ....	1		E. & Mauran, M.	1
1,203,966 (1916)	Bourn, A. O. ....	5	1,342,457 (1920)	Ostromuiskenskii, I.	31
1,204,374 (1916)	Murdoch, H. R. ...	1	1,342,458 (1920)	Ostromuiskenskii, I.	30
1,229,724 (1917)	deMeeus, E. ....	1	1,343,224 (1920)	Molony, S. B. ....	2
1,234,382 (1917)	Peachey, S. J. ....	6	1,349,909 (1920)	Pratt, W. B. ....	1
1,235,850 (1917)	Spence, D. ....	27	1,349,910 (1920)	Pratt, W. B. ....	1
1,235,852 (1917)	Spence, D. ....	27	1,349,911 (1920)	Pratt, W. B. ....	1
1,238,236 (1917)	Whittelsey, T. T. ...	1	1,349,912 (1920)	Pratt, W. B. ....	1
1,239,180 (1917)	Harrison, M. M. ...	1	1,350,824 (1920)	Meyer, E. E. A. G.	2
1,240,116 (1917)	Bernstein, G. ....	1	1,354,123 (1920)	Muntz, W. E. ...	3
1,242,586 (1917)	Ostromuiskenskii, I.	26	1,360,486 (1920)	Worthington, J. V.	
1,242,886 (1917)	Meyer, E. E. A. G.	1		& Hyde, A. W. J.	1
1,247,257 (1918)	Gardner, H. A. ....	1	1,364,055 (1920)	Boggs, C. R. ....	4

1,364,732 (1921)	deLong, C. R. & Watson, W. N. . .	1	1,413,813 (1922)	Twiss, D. F. ....	6
1,365,495 (1920)	Scott, W. ....	1	1,417,970 (1922)	Cadwell, S. M. . .	3
1,370,965 (1921)	Hartong, R. C. . .	2	1,418,166 (1922)	Porritt, B. D. . .	4
1,371,662 (1921)	Bedford, C. W. . .	1	1,418,771 (1922)	Bedford, C. W. & Sibley, R. L. . .	2
1,371,663 (1921)	Bedford, C. W. . .	1	1,418,772 (1922)	Bedford, C. W. . .	4
1,371,664 (1921)	Bedford, C. W. . .	1	1,418,824 (1922)	Naylor, R. B. . .	1
1,372,041 (1921)	Repony, D. ....	4	1,418,825 (1922)	Naylor, R. B. . .	2
1,377,152 (1921)	Bedford, C. W. & Kelly, W. J. ....	1	1,418,976 (1922)	Schidrowitz, P. . .	43
1,379,743 (1921)	Chertoff, G. J. ....	1	1,422,115 (1922)	Martin, R. B. ....	1
1,380,640 (1921)	Davidson, S. C. . .	1	1,422,506 (1922)	Weiss, M. L. ....	2
1,380,765 (1921)	Bedford, C. W. . .	2	1,423,525 (1922)	Hopkinson, E. . .	2
1,381,455 (1921)	Davidson, S. C. . .	1	1,423,526 (1922)	Hopkinson, E. . .	1
1,385,081 (1921)	Lenher, V. ....	1	1,424,020 (1922)	Hopkinson, E. . .	3
1,386,153 (1921)	Bruni, G. ....	1	1,427,283 (1922)	Gibbons, W. A. . .	3
1,388,453 (1921)	Davidson, S. C. . .	1	1,431,455 (1922)	Brown, H. E. & Stover, J. H. . .	1
1,395,413 (1920)	Hoffmann, A. W. & Juve, H. ....	1	1,432,895 (1922)	Plauson, H. ....	2
1,396,837 (1921)	Hartong, R. C. . .	1	1,433,093 (1922)	Ostromuiskenskii, I.	32
1,399,789 (1921)	North, C. O. ....	1	1,433,099 (1922)	Rose, R. P. ....	1
1,400,231 (1922)	O'Brien, W. J. . .	1	1,434,892 (1922)	Harrison, M. M. & Morton, H. A. . .	1
1,405,845 (1922)	Hoffman, H. A. . .	1	1,434,908 (1922)	Morton, H. A. & Harrison, M. M. .	1
1,406,197 (1922)	Levinstein, E. ....	1	1,434,909 (1922)	Morton, H. A. . .	1
1,406,717 (1922)	Bedford, C. W. & Sibley, R. L. . .	2	1,436,894 (1922)	Murrill, P. I. ....	6
1,406,718 (1922)	Bedford, C. W. & Sibley, R. L. . .	3	1,437,487 (1922)	Biddle, A. ....	1
1,406,719 (1922)	Bedford, C. W. & Sibley, R. L. . .	1	1,440,176 (1922)	Ricard, E. ....	1
1,408,826 (1922)	Plauson, H. ....	1	1,440,961 (1922)	Cadwell, S. M. . .	4
1,409,570 (1922)	Pratt, W. B. ....	3	1,440,962 (1922)	Cadwell, S. M. . .	5
1,410,699 (1922)	Martin, R. B. ....	2	1,440,963 (1922)	Cadwell, S. M. . .	6
1,411,231 (1922)	Weiss, M. L. ....	1	1,440,964 (1922)	Cadwell, S. M. . .	7
1,411,786 (1922)	Hopkinson, E. . .	1	1,441,598 (1923)	Mains, G. H. & Phillips, M. ....	1
1,413,172 (1922)	Lorentz, B. E. . .	1	1,443,149 (1923)	Schidrowitz, P. . .	51
1,413,557 (1922)	Phillips, R. O. . .	1	1,445,329 (1923)	Lenher, V. ....	1



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